

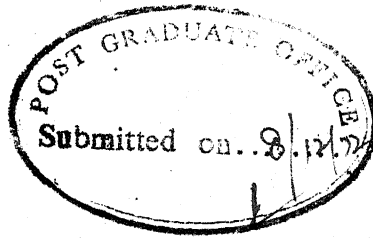
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DEVELOPMENT OF A VAPOR PRESSURE EQUATION AND COMPUTATION  
OF REAL GAS THERMODYNAMIC PROPERTIES OF SELECTED  
REFRIGERANTS AND THEIR MIXTURES

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY

BY  
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to the

DEPARTMENT OF CHEMICAL ENGINEERING  
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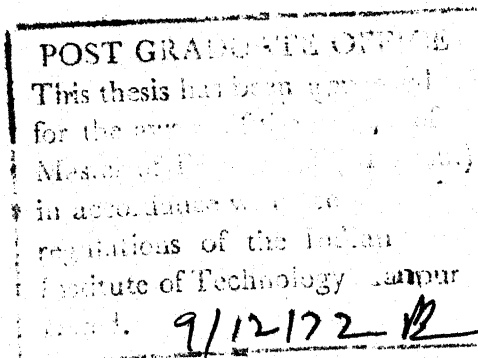
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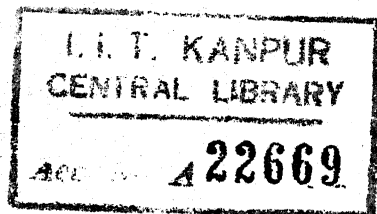
C E R T I F I C A T E

It is certified that this work has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

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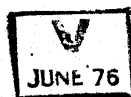


Thesis

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DEDICATED TO MY FRIENDS

B.K. GAIROIA, M.E. KHAN AND PRATIBHA



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V.P. Mundra  
Author

mixtures of ( $\text{CF}_3\text{Cl} + \text{CF}_3\text{H}$ ) and ( $\text{C}_2\text{F}_4\text{Cl}_2 + \text{CFClH}_2$ ). The enthalpy and entropy values are given as isometrics from  $-40^\circ\text{C}$  to  $400^\circ\text{C}$  temperature range and 1-150 atm. pressure range. For  $\text{CH}_3\text{Cl}$ ,  $\text{C}_2\text{F}_2\text{Cl}_2$ ,  $\text{CF}_3\text{Cl}$  our values agree well with the older computed values by DuPont.

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## ABSTRACT

A new vapor pressure equation has been proposed in terms of polynomials in temperature which have been specifically constructed by a weighted Gram-Schmidt orthogonalization procedure. This weighting has been done with a weight function  $e^{-A/T_r}$  which displays the general trend of a vapor pressure temperature relationship. The equation is as follows:

$$P = e^{-A/T_r} (A_0 + A_1 \times T_r + A_2 \times T_r^2 + A_3 \times T_r^3) \quad (1)$$

The proposed equation was tested for 50 different substances for which accurate vapor pressure data were available in the literature from  $T_r = 0.5$  to  $T_r = 1$ . The results were compared with the Ambrose equation (1), the Martin Equation and the K.C.D.C. equation (27). In most cases Eqn.(1) was better than the Martin and K.C.D.C. equations. For Benzene, 2,2,4-trimethyl pentane,  $N_2O$  and  $CH_4$  our results were comparable to those of Ambrose but for methanol, toluene, N-butanol and oxygen Ambrose's equation was better. However Ambrose fitted his equation only from  $T_r$  of 0.6 onwards and adjusted the number of constants (in general 8 to 10) to get the best fit.

Also recent experimental P-V-T and auxiliary data were used to compute real gas thermodynamic properties in the saturated and superheated regions for methyl chloride ( $CH_3Cl$ ), difluorodichloromethane ( $CF_2Cl_2$ ), trifluorochloromethane ( $CF_3Cl$ ), pure compounds and for the azeotropic

## NOMENCLATURE

$A_0, B$	Constants of Clayperon Equation (1)
$A_0, A_1, A_2, A_3, A_4$	Constants of proposed equation (2) and (39)
$A, B, C, D, E, F, G$	Constants of Martin equation of vapor pressure
$a_0, a_1, a_2$	Constants of equation (7)
$a_{00}, a_{11}, a_{12}, a_{21}, a_{22}$	Coefficients of orthogonal polynomials
$a, b$	upper and lower limit of various integrations in vapor pressure section
$A_i, B_i, C_i, a_i, b_i, k_i$	Constants of Martin-Hou equation of state, Eqn. (46).
$C_p$	Specific heat at constant pressure
$E_s(T_r)$	Chebyshev polynomials in $T_r$
$g$	Gibbs energy function
$\Delta H_v$	Heat of Vaporization
$h_T$	Specific enthalpy at $T^\circ K$
$h_T^\circ$	Ideal gas specific enthalpy at $T^\circ K$
$P$	Pressure in atm.
$R$	Gas constant, litre·atm/mole $^\circ K$
$s_T$	Real gas specific entropy at $T^\circ K$ , Kcal/mole $^\circ K$
$s_T^\circ$	Ideal gas specific entropy at $T^\circ K$ , Kcal/mole $^\circ K$
$T_c, P_c, V_c$	Critical temperature, critical pressure, critical volume respectively.
$T_r$	Reduced temperature
$v_g, v_l$	Specific volume of gas and liquid respectively, litre/mole
$W(T_r)$	Weight function
$Z$	Compressibility factor
$\phi_j$	Orthogonal polynomials.
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## CHAPTER 1

### INTRODUCTION

The thesis comprises of two parts, one dealing with the development and testing of a vapor-pressure equation for organic and inorganic compounds and the other involves the computations of real gas thermal properties of some selected halomethanes and haloethanes (F, Cl, Br, I).

The development of the vapor-pressure equation was prompted by Ambrose's article(1) in which he proposed an open ended equation for  $T \ln P$  in terms of independent variable  $T_r$  based on the Chebyshev polynomials ( $E_s(T_r)$ ) having a weight function of  $1/(1-T_r^2)^{1/2}$ . The purpose of the present investigation was to choose a weight function which displays the general behavior of vapor pressure - temperature relationship and using this weight function, to develop polynomials in temperature using the weighted Gram-Schmidt orthogonalization procedure (31) instead of using standard polynomials. After a careful study,  $\exp(-A_0/T_r)$  was chosen as the weight function. Hence in essence what was done was to use the following simple vapor-pressure relationship,

$$\text{Log } P = B - \frac{A_0}{T} \quad \text{or} \quad P = \exp(B) \exp(-A_0/T) \quad (1)$$

and generate correction terms systematically to Eqn.(1) in order to represent the experimental vapor pressure - boiling point data more accurately, from the triple point to the critical point. The proposed equation in terms of orthogonal polynomials in reduced temperature was reduced to the following



form:

$$P = \exp(-A_0/T_r) (A_1 + A_2 T_r + A_3 T_r^2 + A_4 T_r^3 + \dots) \quad (2)$$

Eqn.(2) truncated to 4 terms gave satisfactory results for approximately fifty substances tested and was found to be superior to the IIT-K equation (27) and the Martin Equation (44). Ambrose equation with 8 to 10 terms was found to be better for some compounds than Eqn.(2). The enthalpy of vaporization calculated using Eqn.(2) and the Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_v}{T \Delta v} = \frac{\Delta H_v P}{\Delta z RT^2} \quad (3)$$

showed good agreement with the available experimental data. The constants of Eqn.(2) reported in Table 2 were computed by the least squares orthogonal regression analysis on IBM 7044 Computer using selected experimental data reported in Table 1.

In continuation with our program for the measurement and computation of physical and thermodynamic properties of Halogenated (F,Cl,Br,I) methanes and ethanes (refrigerants), real gas thermodynamic properties such as enthalpy, entropy, etc. are reported here for methyl chloride ( $\text{CH}_3\text{Cl}$ ), difluorodichloromethane ( $\text{CF}_2\text{Cl}_2$ ), Trifluorochloromethane ( $\text{CF}_3\text{Cl}$ ) and azeotropic mixtures ( $\text{CF}_3\text{Cl}$  (50%) +  $\text{CF}_3\text{H}$ ) and ( $\text{CFClH}_2$  (55.1%) +  $\text{C}_2\text{F}_4\text{Cl}_2$ ) using the literature pressure-volume-temperature data. This study was primarily intended to update the existing property tables for  $\text{CH}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$  and  $\text{CF}_3\text{Cl}$  using the most recent literature data over extended temperature and pressure ranges.

Martin-Hou equation of state was used for calculating the departure functions  $(H_T - H_T^0)$ ,  $(S_T - S_T^0)$ , etc., from 230°K to 600°K in the saturated and superheated regions. The values of  $(H_T - H_{ref}^0)$ ,  $(S_T - S_{ref}^0)$  were obtained using the ideal gas heat capacities (60). The reference temperature was taken as -40°C = -40°F.  $(H_T - H_{ref})$  and  $(S_T - S_{ref})$  were obtained by adding  $(H_{ref}^0 - H_{ref})$  and  $(S_{ref}^0 - S_{ref})$  to  $((H_T - H_T^0) + (H_T^0 - H_{ref}^0))$  and  $((S_T - S_T^0) + (S_T^0 - S_{ref}^0))$  respectively.

Binary azeotropic mixture (normally minimum boiling azeotrope) is found to be a 'better' refrigerant than the two pure components forming the mixture. The requisite data were available for the two mixtures ( $CF_3Cl + CF_3H$ ) and ( $CFClH_2 + C_2F_4$   $Cl_2$ ) and hence their thermodynamic properties were also calculated. Experimental measurement of the P-V-T data and other auxiliary data required for the computation of thermodynamic properties are time consuming and cumbersome. It would therefore be desirable to calculate the mixture properties from the pure components using suitable mixing rules. Hence pure component data for  $CF_3Cl$  and  $CF_3H$  were taken, appropriate mixing rules were used (55) and vapor volumes and vapor pressures were calculated for the mixture. These were compared with the experimental mixture data to check the mixing rules. If the agreement between these values is satisfactory, then thermodynamic properties can be calculated using standard thermodynamic procedure.

## CHAPTER 2

### DEVELOPMENT OF THE VAPOR-PRESSURE EQUATION

The fundamental relationship relating the slope of the vapor pressure curve ( $dP/dT$ ) and the enthalpy of vaporization ( $\Delta H_v$ ) is the Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_v}{T \Delta v} \quad (4)$$

Assuming (1) the gas is ideal (2) liquid volume very very small compared to the gas volume (3)  $\Delta H_v$  represented in terms of polynomial in  $T$ , the following general vapor pressure equation is obtained.

$$T \ln P = \sum_{i=1}^N A_i T^{N+1} \quad (5)$$

The Martin equation ( )

$$\ln P = A + \frac{B}{T} + CT + DT^2 + ET^3 + F \log(G-T) \quad (6)$$

can also be represented by Eqn.(5) if  $\log(G-T)$  is represented by polynomial in  $T$  (1).

Let the constants of Eqn.(5) be obtained by the least squares regression analysis. Mathematically the fit should be better when the order of the power series is increased from  $n$  to  $n+1$  where  $n$  is any integer. Due to round off error committed during computation, increasing the order of power series from 2 to  $N$  where  $N$  is the number of data points, a stage comes when increasing the order from  $n$  to  $n+1$  does not improve the fit. This is because equations to

be solved during regression become ill-conditioned. (The equations are called ill-conditioned when they are very sensitive to tiny alterations caused by round off error in their coefficient matrix. The detailed analysis is given in Appendix 1).

Recognising that pressure  $P$  can be represented in terms of polynomials in temperature  $T$  as in Eqn.(5), in calculating the coefficients of the polynomial, the ill-conditioning of the coefficient matrix can be avoided through the least squares orthogonal polynomial fitting procedure (Appendix 1). According to this procedure,  $P$  is expressed in terms of orthogonal polynomials in  $T_r$  as follows:

$$P = W(T_r) \left[ a_0 \phi_0 + a_1 \phi_1 + a_2 \phi_2 + \dots + a_j \phi_j \right]$$

or 
$$P = W(T_r) \sum_{i=0}^N a_i \phi_i \quad (7)$$

where  $W(T_r)$  = weight function

and  $\phi_0, \phi_1, \phi_2, \dots, \phi_j$  are orthonormal polynomials (orthonormal polynomials are orthogonal polynomials with magnitude equal to unity) having the following property.

$$\int_a^b W(T_r) \phi_i \phi_j dT_r = 0 \quad \text{if } i \neq j$$

$$= 1 \quad \text{if } i = j \quad (8)$$

$\phi_0, \phi_1, \phi_2, \dots$  are defined as follows:

$$\phi_0 = \text{orthogonal polynomial of 1st order} = a_{00} \quad (9-a)$$

$$\phi_1 = \text{orthogonal polynomial of IIrd order} = a_{11} + a_{12} T_r \quad (9-b)$$

$$\phi_2 = \text{orthogonal polynomial of IIIrd order} = a_{21} + a_{22} T_r + a_{23} T_r^2 \quad (9-c)$$

and so on

Gram-Schmidt process (Appendix 2) is used to find the coefficients of Eqn.(9). The general relationship given below is used to find out the orthogonal polynomials.

$$\phi_n = \frac{T_r^n - \sum_{m=0}^{n-1} (T_r^n, \phi_m) \phi_m}{\left\| T_r^n - \sum_{m=0}^{n-1} (T_r^n, \phi_m) \phi_m \right\|} \quad (10)$$

where  $(T_r^n, \phi_m)$  = inner product of  $T_r^n$  and  $\phi_m = \int_a^b T_r^n \phi_m W(T_r) dT_r$  (11-a)

$$\left\| T_r^n - \sum_{m=0}^{n-1} (T_r^n, \phi_m) \phi_m \right\| = \left[ \int_a^b \left[ T_r^n - \sum_{m=0}^{n-1} (T_r^n, \phi_m) \phi_m \right]^2 W(T_r) dT_r \right]^{1/2} \quad (11-b)$$

$$\text{and } \phi_0 = \frac{1}{\int_a^b W(T_r) dT_r} \quad (12)$$

Multiplying both sides of Eqn.(7) by  $\phi_j$  and integrating within limits, all terms except  $\int_a^b a_j \phi_j^2 W(T_r) dT_r$  cancel because of the property of orthogonal polynomials given by Eqn.(8).

$$\int_a^b P \phi_j dT_r = \int_a^b a_0 \phi_0 \phi_j W(T_r) dT_r + \int_a^b a_1 \phi_1 \phi_j W(T_r) dT_r + \dots + \int_a^b a_j \phi_j^2 W(T_r) dT_r \quad (13)$$

$$\text{or } a_j = \frac{\int_a^b P \phi_j dT_r}{\int_a^b \phi_j^2 W(T_r) dT_r} \quad (14)$$

Using Eqn.(8), equation (14) can be reduced to the following expression

$$a_j = \int_a^b P \phi_j dT_r \quad (15)$$

The values of  $\phi_0, \phi_1, \phi_2, \dots$  as given <sup>in</sup> Eqn.(9) are substituted

in Eqn.(7) to yield

$$P = W(T_r) * \left[ a_0 a_{00} + a_1 (a_{11} + a_{12} * T_r) + a_2 * (a_{21} + a_{22} * T_r + a_{23} T_r^2) + \dots \right] \quad (16)$$

Eqn.(16) can also be written by grouping the coefficients of  $T_r^i$  as follows:

$$P = W(T_r) * [A_1 + A_2 * T_r + A_3 * T_r^2 + A_4 * T_r^3 + \dots] \quad (17)$$

Hence the main advantage of using the orthogonal polynomials is to avoid ill-conditioning of the coefficient matrix. A second advantage of these polynomials is that the coefficients  $a_0, a_1, a_2, \dots$  of the polynomials are independent of each other. That is the degree of approximation of the polynomial does not have to be chosen at the beginning of the computation. The values of  $a_j$  may be computed successively and the decision of the number of terms to be used can be based on the magnitude of  $a_j$  and the overall fit of the data. In non-orthogonal treatment a change of the degree of the polynomial requires that all coefficients be recomputed, which is not desirable.

Eqn.(17) is the basic form of the proposed vapor pressure equation. The problem now is the choice of the weight function  $W(T_r)$ . Fitting by orthogonal polynomials primarily depends on the selection of weight function. Weight function is the function of independent variable (temperature) and indicates the weightage to be given to the individual points. Moreover it should satisfy the following criteria:

- (a) It should be positive within the integration limits.
- (b) Its integral within the function limit should be positive.

From Hilderbrand (30), the choice of the weight function can be made as follows: If a function can be expressed as

$$y(x) = v(x) \left[ a_0 \phi_0 + a_1 \phi_1 + a_2 \phi_2 \text{ ----} \right] \quad (18)$$

then the choice of  $W(x) \sim v(x)$  can be a useful one.

One such attempt to express vapor pressure in terms of orthogonal polynomials was made by Ambrose who expressed  $T \ln P$  in terms of Chebyshev polynomials. The weight function in case of Chebyshev polynomials is  $1/((T-b)(a-T))^{1/2}$  where  $a$  and  $b$  are the upper and the lower limits of the independent variable  $T$ . As weight function is the measure of weightage given to individual points, Ambrose (1) selected this weight function with a view that as  $T \rightarrow a$  or  $T \rightarrow b$ ,  $W(T) \rightarrow \infty$  giving maximum weightage at the ends. Choice of this weight function gives better fit at the ends of the curve (triple and critical points).

In the present study, the choice of the weight function was made on more realistic approach i.e. from the actual pressure temperature relationship. According to Ramkrishna (57) the best choice of the weight function goes to that function which displays the general trend of the property under investigation. The plot of  $\ln P$  vs  $1/T_r$  is almost a straight line from the triple point to  $T_r = 0.8$  and a S shaped curve from  $T_r = 0.8$  to  $T_r = 1$ . The linear region may be represented by

$$\ln P = B - A_0/T_r \quad (19)$$

$$\text{or } P = \text{EXP}(B) \text{Exp} \left( -\frac{A_0}{T_r} \right) \quad (20)$$

Hence the weightage given to each point can be best represented by  $\exp(-A_0/T_r)$  itself. Hence for the present study the weight function was chosen to be  $\exp(-A_0/T_r)$ . It satisfies the criteria number (a) and (b) as stated before, i.e. weight function is positive and its integration between integration limits ( $T_r$  to 1) is positive.

Also Eqn.(5) can be written as

$$P = \text{Exp}(-A_1/T_r) \text{Exp}(A_2 + A_3 T_r + A_4 T_r^2 + \dots) \quad (21)$$

$$= \text{Exp}(-A_1/T_r) (A'_2 + A'_3 T_r + A'_4 T_r^2 + \dots) \quad (22)$$

From Hilderbrand's criteria as given in Eqn.(18), again the choice of the weight function goes to  $\exp(-A_1/T_r)$  by Eqn.(22).

Substituting  $W(T_r) = \exp(-A_0/T_r)$  in Eqn.(17), the final vapor pressure equation results as given below:

$$P = \exp(-A_0/T_r) (A_1 + A_2 * T_r + A_3 * T_r^2 + A_4 * T_r^3 + \dots) \quad (23)$$

Eqn.(23) was fitted to the experimental data from the literature for 50 compounds by the least squares orthogonal regression analysis.

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## CHAPTER 3

### COMPUTATIONAL PROCEDURE

The problem is to compute the constants  $\Lambda_0$ ,  $a_0$ ,  $a_1$ ,  $a_2$ ,--- and  $a_{00}$ ,  $a_{11}$ ,  $a_{12}$  etc in Eqn.(16).

$$P = \exp(-\Lambda_0/T_r) \left[ a_0 a_{00} + a_1(a_{11} + a_{12} T_r) + a_2(a_{21} + a_{22} T_r + a_{23} T_r^2) + a_3(a_{31} + a_{32} T_r + a_{33} T_r^2 + a_{34} T_r^3) + \dots \right] \quad (16)$$

(i) The initial value of  $\Lambda_0$  was obtained by plotting  $\log P$  vs  $1/T_r$  and taking the slope equal to  $\Lambda_0$ .

(ii)  $a_{00}$ ,  $a_{11}$ ,  $a_{12}$ , ... are given by the following expressions (Eqns. 9, 10 and 12).

$$\phi_0 = a_{00} = \frac{1}{\int_a^b \exp(-\Lambda_0/T_r) dT_r} \quad (24)$$

$$\phi_1 = a_{11} + a_{12} T_r = \left[ T_r - \left\{ \int_a^b \phi_0 T_r \exp(-\Lambda_0/T_r) dT_r \right\} \phi_0 \right] / C \quad (25)$$

$$\text{where } C = \left[ \int_a^b \left\{ T_r - \int_a^b \phi_1 T_r \exp(-\Lambda_0/T_r) dT_r \phi_0 \right\}^2 \exp(-\Lambda_0/T_r) dT_r \right]^{1/2} \quad (26)$$

$$\text{Hence } a_{11} = \left( \int_a^b \phi_0 T_r \exp(-\Lambda_0/T_r) dT_r \right) \phi_0 / C \quad (27)$$

$$a_{12} = a_{11}/C \quad (28)$$

Similarly for  $\phi_2, \phi_3$ ---etc., the above integrations were carried out using the Romberg integration technique (13). In this fashion the values of  $a_{00}$ ,  $a_{11}$ ,  $a_{12}$ ,  $a_{21}$ , etc. were calculated. Here  $a$  and  $b$  are the lower and upper limits of the experimental  $T_r$  data.

(iii)  $a_0, a_1, a_2$  ---- were calculated in the following manner using Eqn.(15). Hence

$$a_0 = \int_a^b P a_{00} dT_r \quad (29)$$

In order to carry out this integration, the pressure P was represented by the following expression:

$$P = \exp \left( A + \frac{B}{T_r} + C T_r + D T_r^2 + E T_r^3 + \dots \right) \quad (30)$$

Using the experimental vapor pressure - boiling point data, constants A, B, C, etc. in Eqn.(30) were computed by the least squares regression analysis. Using Eqn.(30) with the evaluated constants, and  $a_{00}$  value already computed from Eqn.(24), integration of Eqn.(29) was carried out resulting in the value of  $a_0$ .

$$\text{Similarly } a_1 = \int_a^b P(a_{11} + a_{12} * T_r) dT_r \quad (31)$$

Using Eqn.(30) for P and  $a_{11}, a_{12}$  from Eqns. (27) and (28) respectively, the value of  $a_1$  was obtained. In the same fashion values of  $a_2, a_3$  etc. were obtained.

Thus all constants in Eqn.(16) were calculated and a neat expression was obtained for P in terms of  $T_r$ .

For deciding the number of terms required to give the 'best' fit of the experimental data, the following procedure was followed.

Eqn.(16) was truncated after second order polynomial giving Eqn.(32).

$$P = \exp(-A_0/T_r) \left[ a_0 a_{00} + a_1 (a_{11} + a_{12} T_r) \right] \quad (32)$$

Experimental  $T_r$  values were substituted in Eqn.(32) and P calculated for each point and compared with the experimental value. The average and standard deviations of the fit were calculated. If the fit was not satisfactory, additional terms were included in Eqn.(32) and the errors were checked again. This process was continued upto sixth order polynomial. For most of the substances "best" results were obtained using polynomials upto fourth order given below:

$$P = \text{Exp}(-A_0/T_r) \left[ a_0 a_{00} + a_1(a_{11} + a_{12} T_r) + a_2(a_{21} + a_{22} T_r + a_{23} T_r^2) + a_3(a_{31} + a_{32} T_r + a_{33} T_r^2 + a_{34} T_r^3) \right] \quad (33)$$

$$P = \text{Exp}(-A_0/T_r) \left[ (a_0 a_{00} + a_1 a_{11} + a_2 a_{21} + a_3 a_{31}) + (a_1 a_{12} + a_2 a_{22} + a_3 a_{32}) T_r + (a_2 a_{23} + a_3 a_{33}) T_r^2 + a_3 a_{34} T_r^3 \right] \quad (34)$$

$$\text{Let } A_1 = a_0 a_{00} + a_1 a_{11} + a_2 a_{21} + a_3 a_{31} \quad (35)$$

$$A_2 = a_1 a_{12} + a_2 a_{22} + a_3 a_{32} \quad (36)$$

$$A_3 = a_2 a_{23} + a_3 a_{33} \quad (37)$$

$$A_4 = a_3 a_{34} \quad (38)$$

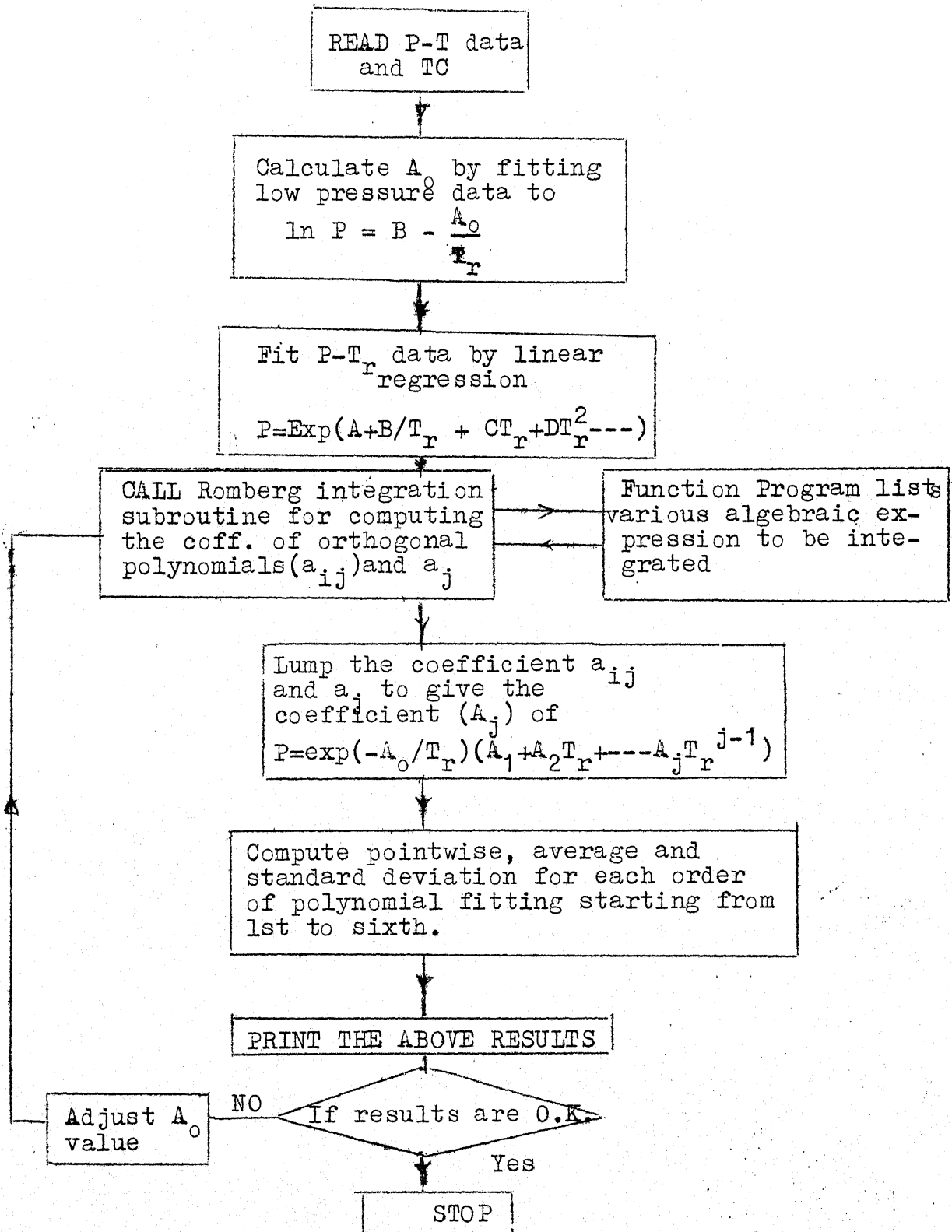
Therefore,

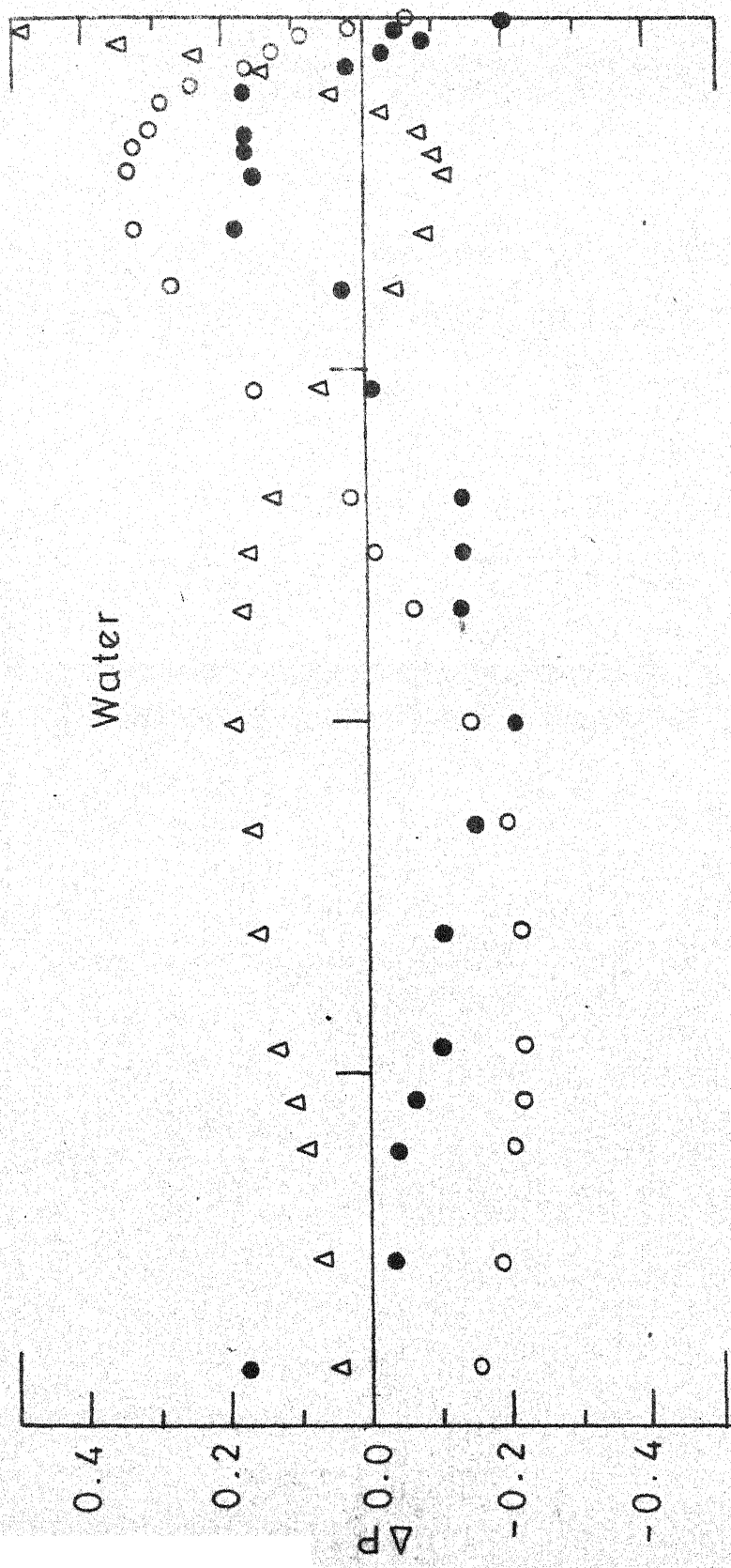
$$P = \exp(-A_0/T_r) A_1 + A_2 T_r + A_3 T_r^2 + A_4 T_r^3 \quad (39)$$

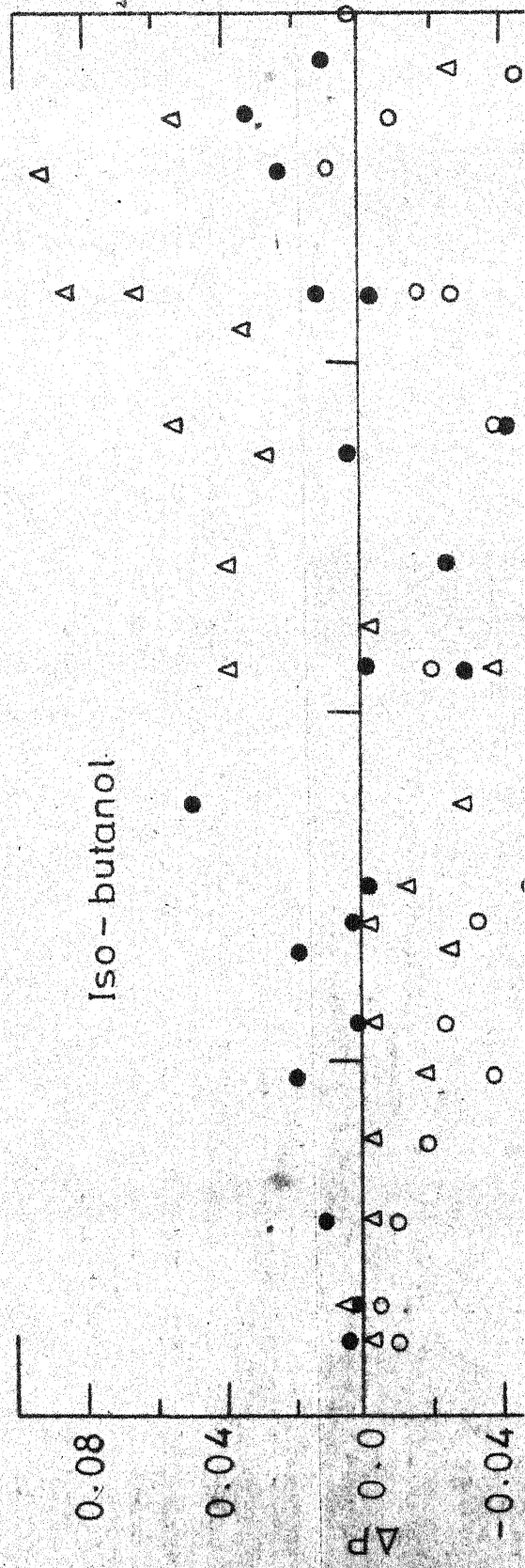
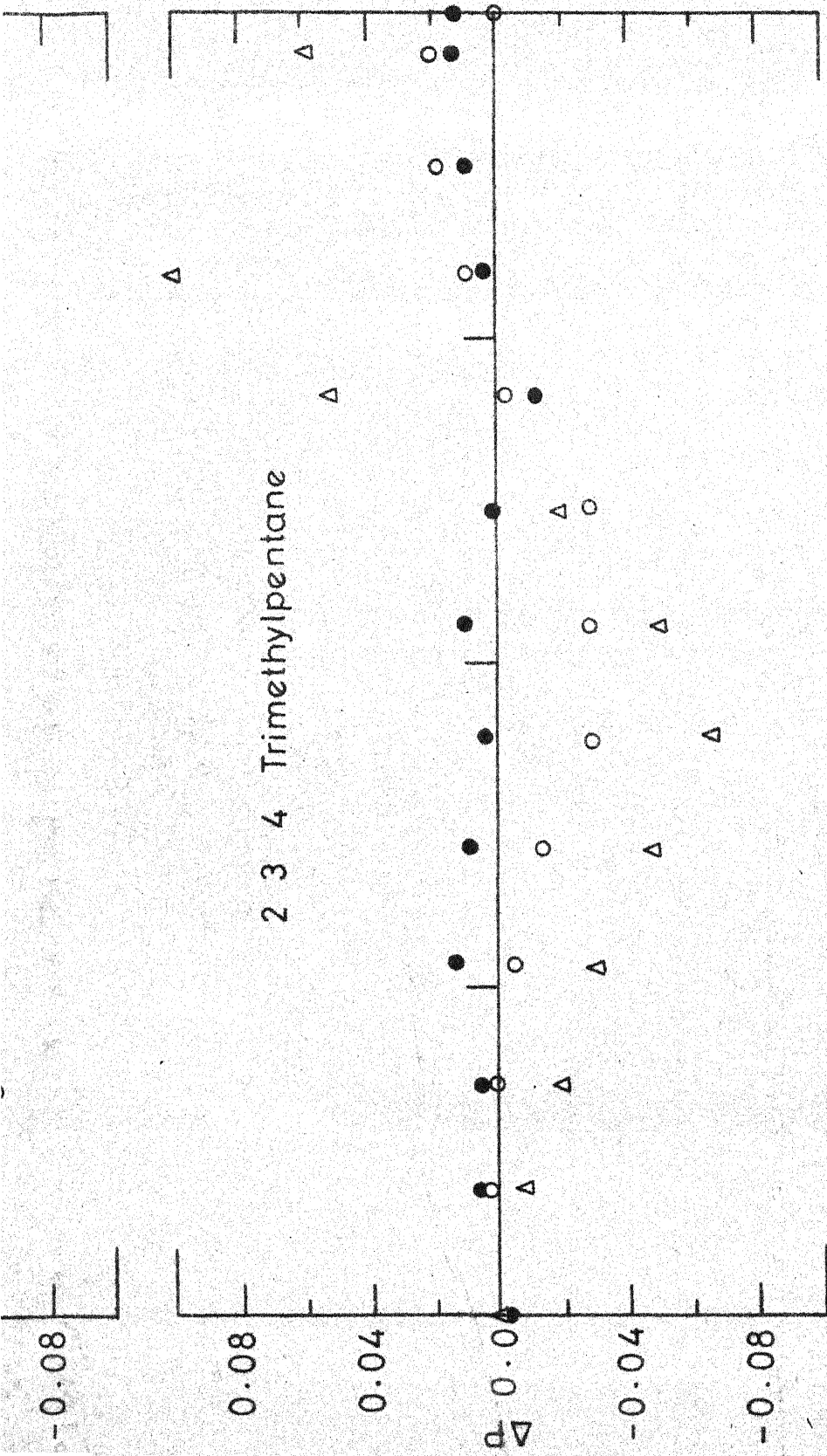
The value of  $A_0$  is then judiciously adjusted by increasing or decreasing the first approximation of  $A_0$  to obtain the 'optimum' fit. Eqn.(39) is the proposed equation.

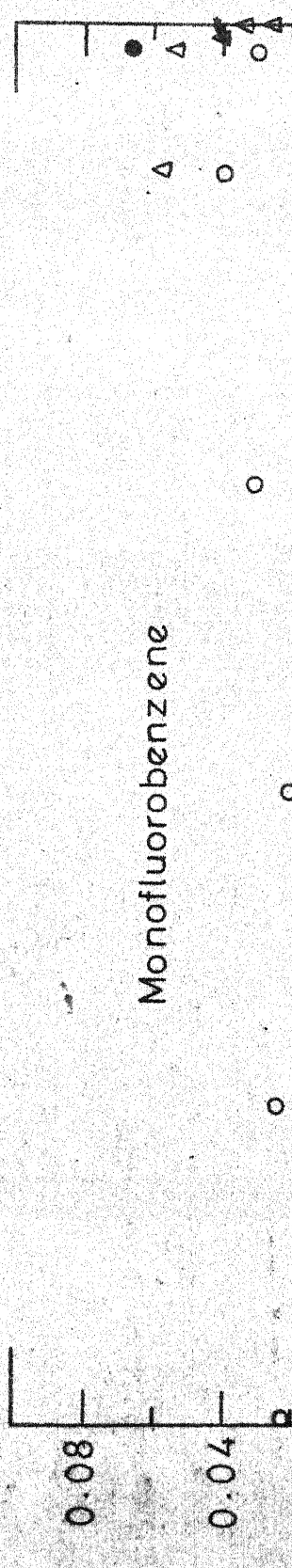
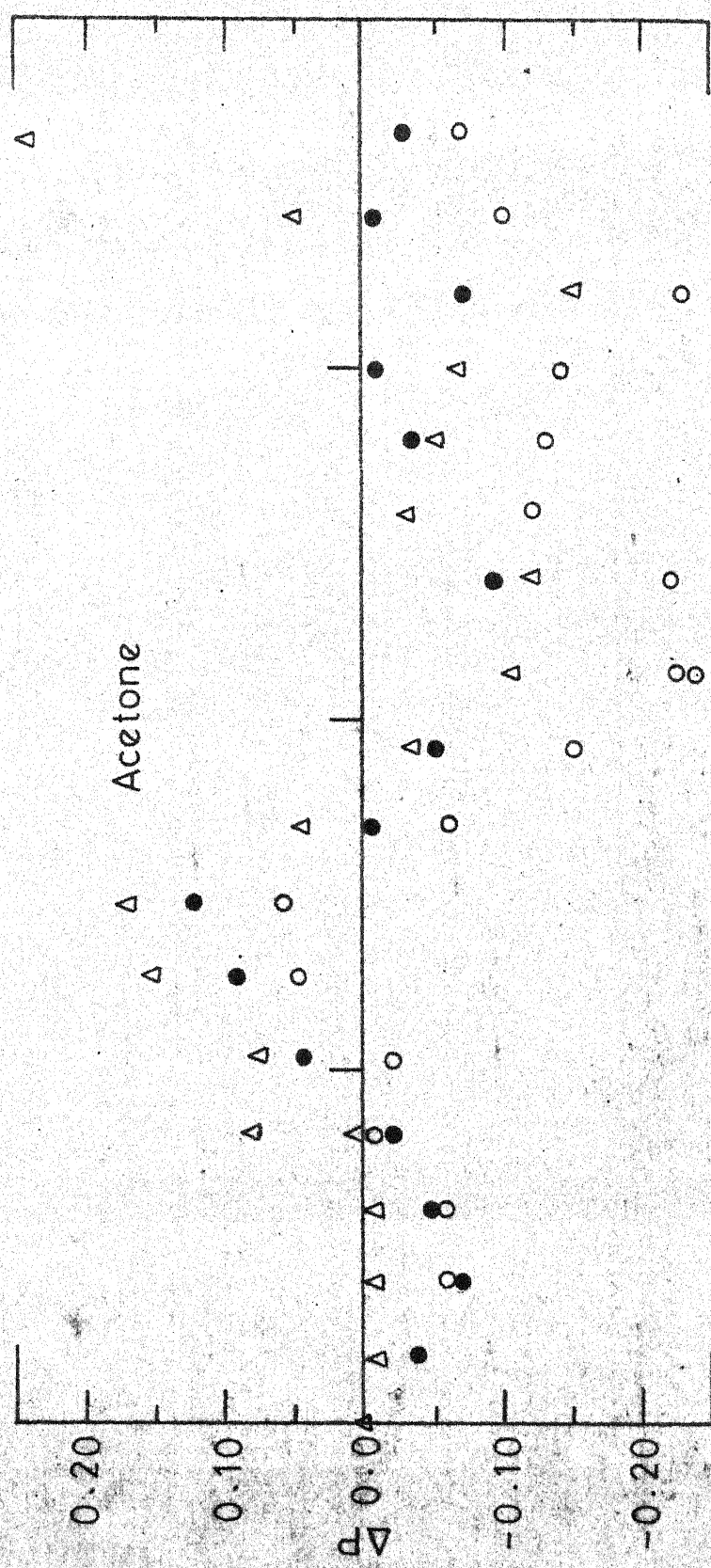
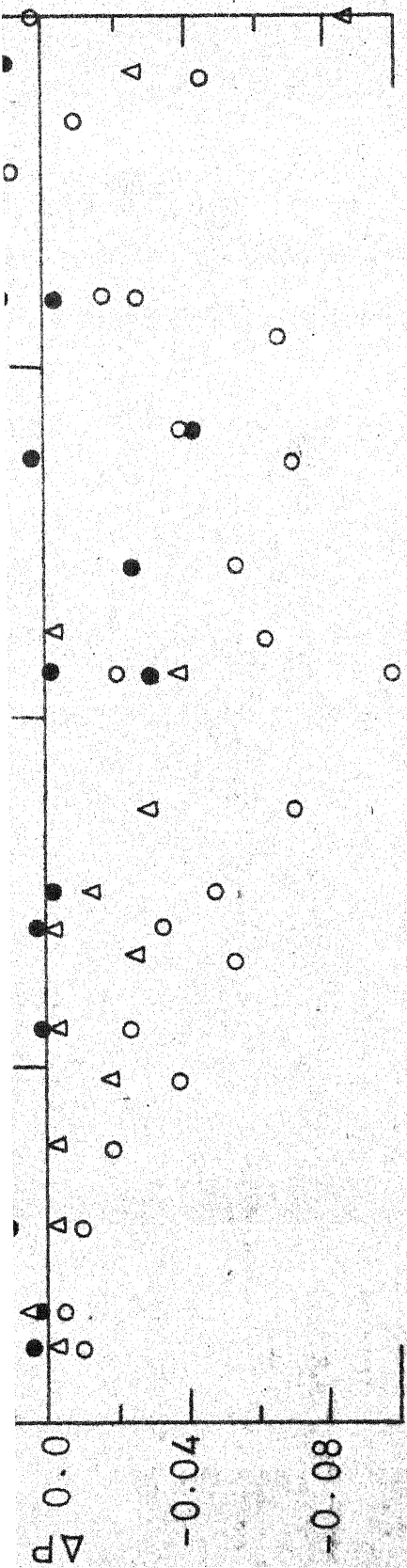
A program in Fortran IV was written to compute the constant of Eqn.(39) using the above procedure. The block diagram is given in Figure (1). The detailed program is given in Appendix 3.

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BLOCK-DIAGRAMFIGURE 1







Monofluorobenzene



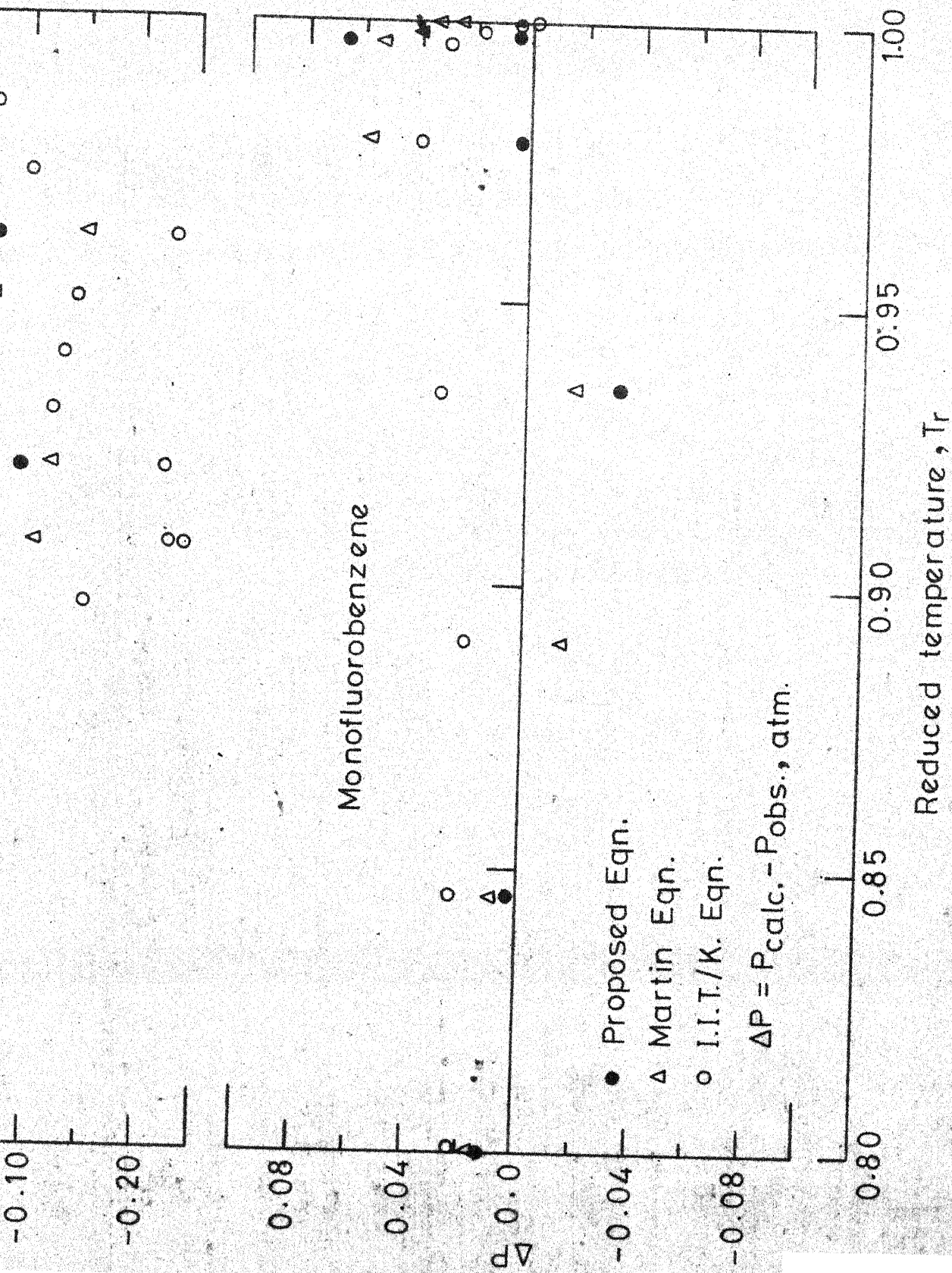


Fig. 2 Deviation plot



## CHAPTER 4

### RESULTS AND DISCUSSION

Results: Experimental data from the literature for Oxygen, water, carbon-monooxide, nitrous oxide, sulfur dioxide and forty five organic compounds were used to test Eqn.(39). The literature data references are given in Table 1. The critical constants were taken from Kudchadker et.al.(39). For each compound the 'optimum' values of  $A_0, A_1, A_2, A_3, A_4$  were calculated and these constants are reported in Table 2. Pointwise fit and the errors for each compound are given in Table 3. The average deviation and the standard deviation were calculated by the following formulae:

$$\text{Average deviation} = \frac{\sum_{i=1}^N |\text{error}|}{N}$$

$$\text{Standard deviation} = \frac{\sum_{i=1}^N [(\text{error})^2]^{1/2}}{N}$$

The enthalpy of vaporization,  $\Delta H_V$  for each compound at 25°C and at the normal boiling point (at 760 mm Hg pressure) were calculated using the Clapeyron equation, Eqn.(4).

$$H_V = T \Delta v \left( \frac{dP}{dT} \right) = T(v_g - v_l) \left( \frac{dP}{dT} \right) = \frac{RT^2 \Delta Z}{P} \frac{dP}{dT} \quad (42)$$

The  $\frac{dP}{dT}$  values were calculated from Eqn.(39) and  $\Delta Z$  values from Haggmacher's equation given below

$$Z = \left[ 1 - \frac{P_r}{T_r^3} \right]^{1/2} \quad (43)$$

The final equation used for  $H_V$  calculations is given by Eqn.(44).

$$\Delta H_V = \frac{RT^2}{P} \left(1 - \frac{P_r}{T_r^3}\right)^{1/2} \left[ \exp(-A_0/T_r) \left( A_2/T_c + 2A_3T_r/T_c + 3A_4T_r^2 \right) + PA_0/T_r^2 T_c \right] \quad (44)$$

These calculated  $\Delta H_V$  values are compared with the available experimental values in Table 1.

Discussion: In general Eqn.(39) represents the experimental data from the triple point to the critical point quite satisfactorily. Further, Eqn.(39) was compared with the Martin (44) IIT-K (27), and Ambrose (1) equations. The comparison is reported in Table 4 in terms of the average and standard deviations. For most of the compounds Eqn.(39) was found to be superior to the Martin and IIT-K equations. Ambrose tested his equation

$$T \log P = \sum_{S=0}^n a_s E_s(x) \quad (45)$$

where  $E_s(x)$  = Chebyshev polynomials

$$x = 2T - (T_{\max} + T_{\min}) / (T_{\max} - T_{\min})$$

for oxygen, nitrous oxide, methane, 2-2-4 trimethylpentane, benzene, toluene, methanol and n-butanol. Ambrose reported the deviations from the experimental value in terms of  $\ln(P_{\text{calc}}/P_{\text{actual}})$  which varied from  $\pm 0.0004$  to  $\pm 0.001$  using Eqn.(45). For nitrous oxide, methane, 2-2-4 trimethylpentane, and benzene Eqn.(39) with five constants was comparable to Ambrose eight constant equation. However, for other compounds Eqn.(39) was not as good as the Ambrose equation. In general Ambrose used eight to ten terms in

Eqn.(45) to fit the data. Fig. 2 reports the deviations in  $\Delta P = P_{\text{calc}} - P_{\text{obs}}$  for six compounds by Eqn.(39), Martin and IIT-K equations for the region  $0.8 \leq T_r \leq 1.0$ . Except for acetone, the deviations are random and smaller than by other two models.

Hence, a five constant vapor pressure equation has been proposed based on the general vapor pressure-temperature behaviour, which fits the experimental data from  $T_r = 0.6$  upto the critical within 0.1 per cent. In general, it is better than Martin's seven constant equation and IIT/K four constant equation. Ambrose equation with eight to ten constants is slightly better. Eqn.(39) can be used with confidence for the calculation of  $\Delta H_v$  values and for design calculations.

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## CHAPTER 5

### REAL GAS THERMODYNAMIC PROPERTIES

The literature survey on experimental pressure-volume-temperature data for compounds of our interest revealed that more recent reliable data were available for methyl chloride ( $\text{CH}_3\text{Cl}$ ), difluorodichloromethane ( $\text{CF}_2\text{Cl}_2$ ), trifluorochloromethane ( $\text{CF}_3\text{Cl}$ ) and for azeotropic mixtures of trifluorochloromethane with trifluoromethane ( $\text{CF}_3\text{Cl}$  (50%) +  $\text{CF}_3\text{H}$  (50%)) and monofluoromonochloromethane with tetrafluorodichloroethane ( $\text{CFClH}_2$  (55.1%) +  $\text{C}_2\text{F}_4\text{Cl}_2$ ). The real gas thermodynamic properties for  $\text{CH}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$  and  $\text{CF}_3\text{Cl}$  have already been computed by DuPont (20) using older data. It was therefore decided to use the newer data and compute the real gas thermodynamic properties, such as, enthalpy, entropy etc., for these compounds using the standard procedure (44). It is felt that these newer derived properties would result in "better" equipment design.

The application of azeotropic mixture to conventional refrigeration systems has resulted in improved coefficient of performance. A knowledge of the thermodynamic properties of azeotropic refrigerant mixtures is thus essential to explore the potential of new mixed refrigerants and for the analysis and design of modern refrigeration systems. An azeotropic mixture has thermodynamic characteristics which for all practical purposes are similar to those of the pure components. This enables their basic properties to be computed using the

procedure for the pure components as developed in Chapter 6. In order to use this procedure one must carry out elaborate experimental investigations for the determination of P-V-T data and the vapor pressure data. One could avoid this by developing a procedure for calculating thermodynamic properties of mixtures based upon the properties of pure components forming the mixture. One such procedure as developed by Piacentini and Stein (55) is tried here based upon certain mixing rules described in the later chapter. This procedure is tested for  $\text{CF}_3\text{Cl} + \text{CF}_3\text{H}$  mixture.

As a consequence of this work, a "Thermodynamic Package" computer program has been developed for computing the thermodynamic properties of pure compounds and their mixtures, using the minimum computer time.

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## CHAPTER 6

### COMPUTATIONAL PROCEDURE

The computation of real gas thermodynamic properties depends upon the availability of the following information:

1. Equation of state representing accurately, experimental pressure-volume-temperature data.
2. Vapor pressure-boiling point data
3. Liquid density vs temperature
4. Enthalpy of vaporization as function of temperature
5. Ideal gas heat capacity as function of temperature
6. Departure-functions calculations

The accuracy of derived thermodynamic properties depends primarily upon the accuracy of the experimental P-V-T data. For example, if the P-V-T measurements yield compressibilities accurate to 0.1%, then the thermal functions are generally accurate to about 5-10% because the calculation procedure involves differentiation twice and integration once. Hence one must choose an equation of state which represents reliable experimental data better than 0.1% over the range of pressures and temperatures under investigation.

1. After a careful and detailed study, the Martin-Hou equation (40) was chosen for the present study. The Martin-Hou equation, Eqn.(46), was derived after a systematic study of a large number of compounds both polar and non-polar and it has been successfully applied to halogenated methanes and ethanes.

$$P = \frac{RT}{v-b} + \sum_{i=2}^5 \frac{f_i(T)}{(v-b)^i} + \frac{f_6(T)}{e^{av}} + \frac{f_7(T)}{e^{2av}} \quad (46)$$

where  $f_i(T) = A_i + B_i T + C_i \exp(-kT/T_c)$

$f_6(T) = A_6 + B_6 T + C_6 \exp(-kT/T_c)$

$f_7(T) = A_7 + B_7 T + C_7 \exp(-kT/T_c)$

The region for each compound selected for the present investigation is depicted in Fig.(3). This vapor region is the one normally involved in the refrigeration calculations. Eqn.(46) truncated after five terms was found suitable to represent the available data with the precision and accuracy required in the present study. The last two terms are usually required to represent data in very high density regions.

2. In order to represent experimental vapor pressure-boiling point data accurately, the following two equations were selected.

$$\log P = A + \frac{B}{T} + CT + DT^2 \quad (47)$$

$$P = \exp(-A_0/T_r) \left[ A_1 + A_2 T_r + A_3 T_r^2 + A_4 T_r^3 \right] \quad (39)$$

Eqn.(47) was used because the constants A,B,C,D were already available in the literature. For other compounds Eqn.(39) was used.

3. Liquid densities were calculated using Yen and Woods procedure (68). It has been demonstrated (68) that this procedure predicts liquid densities generally within 1% and is convenient for machine computations.

4.  $\Delta H_v$  was calculated as follows:

$$(h_T - h_T^0) = Pv - RT + \sum_{i=2}^5 \frac{A_i + (kT_r + 1) C_i \exp(-kT_r)}{(i-1)(v-b)^{i-1}} \quad (57)$$

(b) Entropy ( $s_T - s_T^0$ )

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(-\frac{\partial p}{\partial T}\right)_v \quad (58)$$

$$ds \Big|_T = \left(\frac{\partial p}{\partial T}\right)_v dv \Big|_T \quad (59)$$

If  $P^0$  is the very low pressure where gas behaves ideally, then

$$s(P^0, \text{atm}) - s(P, \text{atm}) = - \int_v^{v^0} \left(\frac{\partial p}{\partial T}\right)_v dv \quad (60)$$

If gas behaves ideally also at  $P$  atm, then  $(\partial p / \partial T)_v = \frac{R}{v}$ .

$$\text{Hence } s^0(P, \text{atm}) - s^0(P^0, \text{atm}) = - \int_v^{v^0} \frac{R}{v} dv = + \int_v^{v^0} \frac{R}{v} dv \quad (61)$$

where  $s^0$  represents ideal entropy at  $P$ , atm and  $T$ .

Adding Eqn.(61) to Eqn.(60), we get

$$s^0(P, \text{atm}) - s(P, \text{atm}) = - \int_v^{v^0} \left(\frac{\partial p}{\partial T}\right)_v dv + \int_v^{v^0} \frac{R}{v} dv \quad (62)$$

$$\text{or } s(P, \text{atm}) - s^0(P, \text{atm}) = \int_v^{v^0} \left[ \left(\frac{\partial p}{\partial T}\right)_v - \frac{R}{v} \right] dv \quad (63)$$

substituting Eqn.(55) into Eqn.(63) we obtain  $v^0 \rightarrow \infty$ ,

$$\begin{aligned} s(P, \text{atm}) - s^0(P, \text{atm}) &= R \ln(v-b) - R \ln(v^0-b) - \left[ \frac{B_2}{v-b} \right. \\ &+ \frac{B_3}{2(v-b)^2} + \frac{B_4}{3(v-b)^3} + \frac{B_5}{4(v-b)^4} \Big] + \left[ \frac{C_2}{v-b} + \frac{C_3}{2(v-b)^2} + \frac{C_4}{3(v-b)^3} \right. \\ &+ \frac{C_5}{4(v-b)^4} \Big] \left[ k \exp(-kT_r/T_c) \right] - R \ln v + R \ln v^0 \end{aligned} \quad (64)$$

because  $v^0$  is much larger than  $b$  and hence  $(v^0-b) \approx v^0$ .

(c) Real Gas Properties with respect to Reference Temperature of  $-40^\circ\text{C} = -40^\circ\text{F}$ .

The path for calculation of enthalpy demonstrated in



Fig.4 is given below:

1. Enthalpy of saturated liquid at reference temperature is zero,  $h_1 = 0$ .

(2) Heat the saturated liquid at  $-40^\circ\text{C}$  to saturated vapor at  $-40^\circ\text{C}$ .

$$h_1 = h_1 + \Delta h_v \Big|_{-40^\circ\text{C}} \quad (65)$$

(3) Decrease pressure of vapor from its vapor pressure  $P$  to zero pressure at  $-40^\circ\text{C}$ .

$$h_{12} = - (h - h^0)_{-40^\circ\text{C}} \quad (66)$$

$$h_2 = h_1 + h_{12} = h_1 + \Delta h_v \Big|_{-40^\circ\text{C}} - (h - h^0)_{-40} \quad (67)$$

(4) Heat vapor from  $-40^\circ\text{C}$  to temperature  $T$  at zero pressure

$$h_{23} = \int_{-40}^T C_p^0 dT \quad (68)$$

hence 
$$h_3 = h_1 + h_{12} + h_{23} = h_1 + \Delta h_v \Big|_{-40} - (h - h^0) + \int_{-40^\circ\text{C}}^T C_p^0 dT \quad (69)$$

(5) Increase pressure of vapor from zero pressure to pressure  $P$

$$h_{3g} = (h_T - h_T^0) \quad (70)$$

$$\begin{aligned} \therefore h_g &= h_1 + h_{12} + h_{23} + h_{3g} \\ &= h_1 + \Delta h_v \Big|_{-40^\circ\text{C}} - (h - h^0)_{-40^\circ\text{C}} + \int_{-40^\circ\text{C}}^T C_p^0 dT \\ &\quad + (h_T - h_T^0) \end{aligned} \quad (71)$$

where 
$$\int_{T_{\text{ref}}}^T C_p dT = B_1(T - T_{\text{ref}}) + B_2 \log(T/T_{\text{ref}}) + B_3(1/T_{\text{ref}} - 1/T) + B_4(T^2 - T_{\text{ref}}^2)/2 + B_5(T^3 - T_{\text{ref}}^3)/3 + B_6(T^4 - T_{\text{ref}}^4)/4 \quad (72)$$

The calculation procedure of entropy at any point as demonstrated in Fig.5 is given below:

$$(s_T - s_{ref}) = (s_T - s_2) + (s_2 - s_{ref}) \quad (73)$$

$$(s_T - s_2) = (s_T - s_2') + (s_2 - s_2') \quad (74)$$

$$= (s_T - s_T^0) + (s_T^0 - s_2') + (s_2 - s_2^0) + (s_2^0 - s_2') \quad (75)$$

Since  $s_2' = s_2^0$  (at low pressure)

$$(s_T - s_2) = (s_T - s_T^0) + (s_T^0 - s_2^0) - (s_2^0 - s_2^0) + (s_2 - s_2^0) \quad (76)$$

$$= (s_T - s_T^0) + R \ln \frac{P}{P^0} - R \ln \frac{P_{ref}}{P^0} + (s_2 - s_2^0) \quad (77)$$

$$= (\text{departure function at temperature } T \text{ and Pressure } P) - R \ln \frac{P}{P_{ref}}$$

$$- (\text{departure function at temperature } T \text{ and pressure } P_{ref}) \quad (78)$$

$$(s_2 - s_{ref}) = (s_2 - s_2^0)_T + (s_2^0 - s_{ref}^0) + (s_{ref}^0 - s_{ref})_{T_{ref}} \quad (79)$$

$$= (s_2 - s_2^0)_T + \int_{T_{ref}}^T \frac{C_p dT}{T} - (s_{ref} - s_{ref}^0)_{T_{ref}} \quad (80)$$

$$\begin{aligned} \text{where } \int \frac{C_p dT}{T} &= B_1 \times \log \frac{T}{T_{ref}} + B_2(1/T_{ref} - 1/T) \\ &+ B_3(1/T_{ref}^2 - 1/T^2)/2 + B_4(T - T_{ref}) \\ &+ B_5(T^2 - T_{ref}^2)/2 + B_6(T^3 - T_{ref}^3)/3 \end{aligned} \quad (81)$$

The Gibbs energy function  $\frac{g - g^0}{T}$  can be calculated as follows:

$$g = h - Ts \text{ or } \frac{g}{T} = \frac{h}{T} - S \quad (82)$$

$$\left(\frac{g - g^0}{T}\right) = \left(\frac{h - h^0}{T}\right) - (s - s^0) \quad (83)$$

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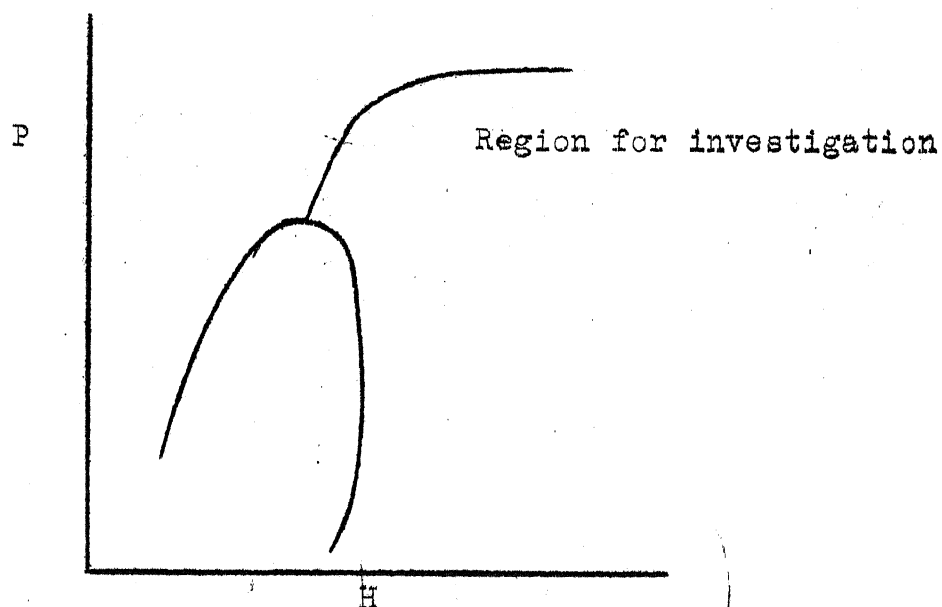


FIGURE: 3

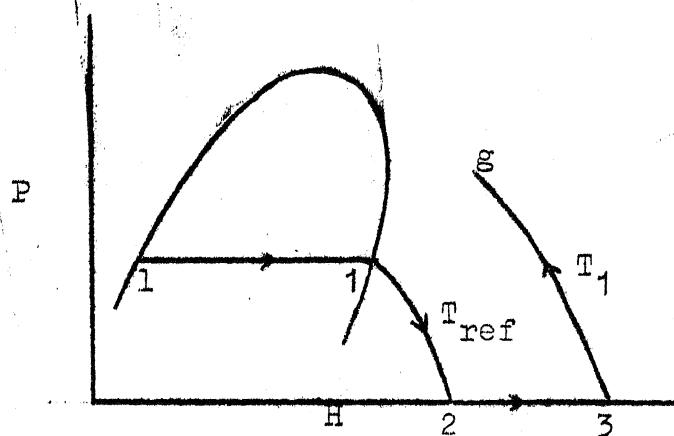


FIGURE:4: PATH FOR CALCULATION OF ENTHALPY

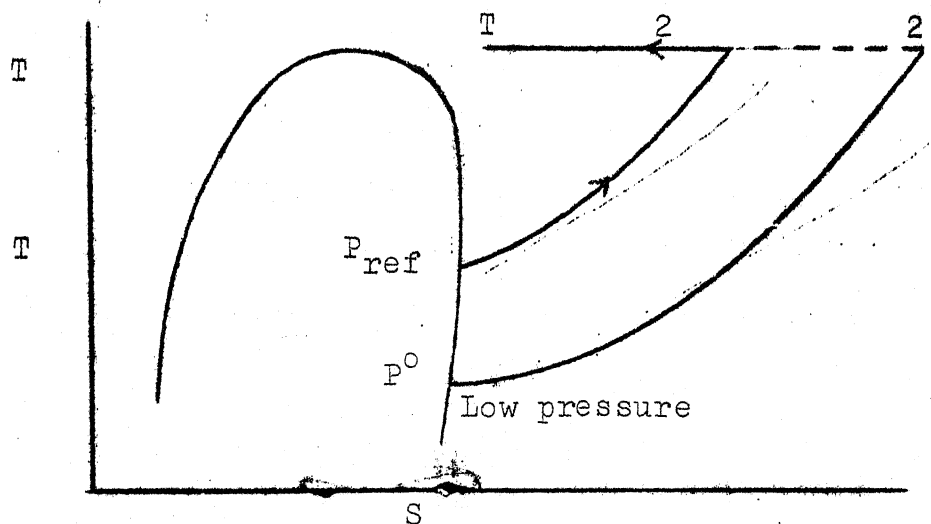


FIGURE 5: PATH FOR CALCULATION OF ENTROPY

## CHAPTER 7

### DESCRIPTION OF COMPUTER PROGRAM

1. Main: This program fits the P-V-T data to Eqn.(46) by linear regression. Approximate values of b and k were assumed and average and standard errors were computed. The fit giving the least standard error was taken to be the "best" fit. The Main calls the subroutine Thermo.
2. Thermo: This subroutine first fits the vapour pressure data. Then for any temperature and pressure, the volume of saturated vapor is calculated from Martin equation by Newton-Raphson technique (13). Liquid volume is calculated from subroutine LQDN. Heat of vaporization is calculated from Clapeyron equation. Since volume term is in the denominator in Eqn. (46) it is difficult and time consuming to calculate v for different set of P and T values. Hence this subroutine reads the volume at which we want to calculate the thermal functions. This subroutine calls ENTHA, ENTRO, HRS to calculate departure functions, ideal gas enthalpy and ideal gas entropy at any temperature and pressure. Main uses Eqn.(71) and (73) to calculate real gas enthalpy and entropy with respect to datum temperature at  $-40^{\circ}\text{C}$ .
3. ENTHA: This subroutine calculates enthalpy departure by Eqn.(57) at any pressure P and temperature T.
4. ENTRO: This subroutine calculates entropy departure by Eqn.(64) at any pressure P and temperature T.
5. LQDN: This subroutine calculates saturated liquid volume by Yen and Wood correlation (68).

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## CHAPTER 8

### RESULTS AND DISCUSSIONS

The sources of data used for the pure compounds and mixtures selected, are given in Table 5. For each compound, constants of the Martin-Hou equation, vapor pressure equation and the heat capacity correlation are given in Tables 6 through 10. The computer program listing given in Appendix IV was used to calculate the thermodynamic properties in the saturated and superheated regions. The same equations and the program were used for the two azeotropic mixtures because an azeotropic mixture behaves as a single component. For the ideal gas heat capacity of the mixture, the following formula was used.

$$C_{Pm} = y_1 C_{p_1} + y_2 C_{p_2}$$

The thermodynamic properties are presented in Tables 11 through 13 for the compounds investigated at 10 deg. temperature interval from -40°C to + 400°C at definite selected volumes. Attempts were made to minimize the computational time while ensuring that the accuracy of results is not affected. The programs have been rendered flexible and are general in nature.

The properties have been presented in units consistent with the international conventions. The present values are compared with the DuPont values in Table 11 for methylchloride, difluorodichloromethane and trifluorochloromethane.

## CHAPTER 9

### PREDICTION PROCEDURE FOR MIXTURES

#### Mixing Rules:

1. Equation of State: For binary mixtures, the following equation has been used for determining mixture constants from pure component constants.

$$P_m = y_1^2 P_{11} + 2y_1 y_2 P_{12} + y_2^2 P_{22} \quad (84)$$

where  $P_m$  = mixture constant

$y_1, y_2$  = mole fraction of the  $i$ th component

$P_{11}, P_{22}$  = pure component constants

$P_{12}$  = interaction constant

The problem is to find an expression for  $P_{12}$ . Piacentini and Stein (55) found that the following mixing rules for  $P_{ij}$  predicted the mixture properties very satisfactorily for fluorocarbon system. These were adopted in the present study.

$$P_{ij} = \frac{2 P_{ii} P_{jj}}{P_{ii} + P_{jj}} \quad \text{for } A_2, C_2 \quad (85)$$

$$= \frac{(P_{ii}^{1/3} + P_{jj}^{1/3})^3}{8} \quad \text{for } \begin{array}{l} A_i, i = 3, 6 \\ C_i, i = 3, 6 \end{array} \quad (86)$$

$$= (P_{ii} P_{jj})^{1/2} \quad \text{for } \begin{array}{l} B_i, i = 2, 6 \\ k, a, T_c \end{array} \quad (87)$$

$$= (P_{ii} + P_{jj})/2 \quad \text{for } b \quad (88)$$

These rules enable the Martin-Hou constants to be determined for a given concentration of a mixture.

2. Vapor Pressure Equation: The vapor pressures of both components of the mixture must be fitted to identical model. The following mixing rule (62) yields results with a maximum error within three percent over the entire temperature range for some fluorocarbon mixtures:

$$P_{ij} = 3 (P_{ii} + P_{jj})/4 \quad (89)$$

Using this mixing rule, constants of Eqn.(39) for the mixture ( $\text{CF}_3\text{Cl}$  (50%) +  $\text{CF}_3\text{H}$ ) were calculated.

3. Heat capacity of the mixture was calculated using Eqn.(60).

The constants of the Martin-Hou equation, the vapor pressure equation, and the heat capacity equation are given in Table 12 for  $\text{CF}_3\text{Cl}$ (50%) +  $\text{CF}_3\text{H}$  mixture.

#### Results:

The Martin-Hou equation of state for the mixture was used to calculate pressure at specific temperature and volume and compared with the experimental values in Table 13. As seen from this table, the agreement is satisfactory at volumes greater than critical volume. Hence the selected mixing rules for the Martin-Hou constants are satisfactory.

The vapor pressure equation for the mixture however, did not give good results. The values computed for the mixture are compared with the experimental values in Table 14. It is therefore necessary to choose better mixing rules for the

vapor pressure equation constants.

As we do not have "proper" mixing rules for the prediction of mixture equations, the calculation of thermodynamic function was not attempted.

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## CHAPTER 10

### CONCLUSION

It is hoped that (1) the proposed vapor pressure equation will be of use for scientists and engineers for the calculation of vapor pressures from the triple point to the critical point. (2) The calculated real gas properties for three pure compounds and two mixtures will prove useful for engineers in designing "better" refrigeration systems. The author did not have much success with the prediction of mixture properties from pure component data. Systematic work on mixing rules is necessary for this purpose.

# REFERENCES

1. Ambrose, D., J.F. Counsell, and A.J. Davenport, J.Chem. Thermo., 2, 283 (1970).
2. Ambrose, D., J.Chem.Soc., (A), 381, (1968).
3. Ambrose, D., B.E. Broderick, and R.Townsend, J.Chem.Soc., (A), 633 (1967).
4. Ambrose, D., and R.Townsend, J.Chem.Soc., (A), 3614 (1963).
5. Ambrose, D., J.D.Cox, and R.Townsend, Trans.Faraday Soc., 56, 452 (1960).
6. Armstrong, G.T., F.G. Brickwedde, and R.B.Scott, J.Res. Natl. Bur. Std., 55, 39 (1955).
7. Barron, C.H., Jr., J.C. Chaty, R.A. Gonzalez, and J.W.Eldridge, J.Chem.Eng. Data, 7, 394 (1962).
8. Beattie, J.A., and S. Marple Jr., J.Am.Chem.Soc., 72, 1449 (1950).
9. Beattie, J.A., S.W. Levine, and D.R. Douslin, J.Am.Chem.Soc., 73, 4431 (1951).
10. Bender, P., G.T. Furukawa, and J.R. Hyndman, Ind.Eng.Chem., 44, 387 (1952).
11. Berthoud, A., J.Chim. Phys., 15, 3 (1917).
12. Brown, J.A., Ind.Eng.Chem., 32, 836 (1940).
13. Carnahan, B., J.A. Luther and J.O. Wilkes, Applied Numerical Methods, New York, Wiley (1969).
14. Clayton, J.O., and W.F. Giaque, J.Am.Chem.Soc., 54, 2610 (1932).
15. Collerson, R.R., J.F. Counsell, R. Handley, J.J. Martin, and C.H.S. Sprake, J.Chem.Soc., 3697 (1965).
16. Connolly, J.F., J. Phys. Chem., 66, 1082 (1962).
17. Couch, E.J. & K.A. Kobe, J.Chem.Eng. Data, 6, 229 (1961).

18. Crowder, G.A., Z.L. Taylor, T.M. Reed, and J.A. Young, J. Chem. Eng. Data, 12, 481 (1964).
19. Douslin, D.R., R.T. Moore, and G. Waddington, J. Phy. Chem., 63, 1959 (1959).
20. E.I. DuPont de Nemours & Company (Inc.), "Thermodynamic Properties of Methyl Chloride", (1939).
21. = E.I. Du Pont de Nemours & Company (Inc.), "Thermodynamic Properties of Difluorodichloromethane" T-12T, (1956).
22. E.I. Du Pont de Nemours & Company (Inc.), "Thermodynamic Properties of Trifluorochloromethane", T-13, (1959).
23. Eucken, A., and W. Berger, Z. Ges. Kalte- und., 41, 145 (1934).
24. Evans, F.D., P.F. Tiley, J. Chem. Soc., A, 134 (1966).
25. Forziati, A.F., W.R. Norris and F.D. Rossini, J. Res. Natl. Bur. Std., 43, 555 (1949).
26. Furukawa, G.T., R.E. McCoskey, and M.L. Reilly, J. Res. Natl. Bur. Std., 52, 11 (1954).
27. Goyal, V.K., "A New Three Constant Vapor Pressure Equation", Master's thesis, Dept. of Chem. Engg., IIT-Kanpur, (1971).
28. Gordon, J., and W.F. Giauque, J. Am. Chem. Soc., 70, 1506 (1948).
29. Hestermans, P., and D.J. White, J. Phys. Chem., 65, 362 (1965).
30. Hilderbrand, F.B., Introduction to Numerical Analysis, Tata McGraw-Hill Publishing Co., Bombay-New Delhi, 1st Ed., (1956).
31. Hilderbrand, F.B., 'Methods of Applied Mathematics' 2nd Ed., Prentice-Hall (1965).
32. Hoge, H.J., J. Res. Natl. Bur. Std., 34, 281 (1945).
33. Hsu, C.C. and McKetta, J.J., J. Chem. Eng. Data, 9(1), 45 (1964).
34. Kay, W.B., Ind. Eng. Chem., 32, 358 (1940).
35. Kay, W.B., J. Am. Chem. Soc., 68, 1336 (1946).

36. Kay, W.B., and W.E. Donham, Chem.Eng.Sci., 4, 1(1955).
37. Kang, T.L., L.J. Hirth, and J.J. McKetta, J.Chem.Eng. Data, 6, 220 (1961).
38. Kobe, K.A., H.R.Crowford, and R.W. Stephenson, Ind.Eng.Chem., 47, 1762 (1955).
39. Kudohadker, A.P., G.H.Alani, and B.J.Zwolinski, Chem.Rev. 68, 659 (1968).
40. Martin, J.J., Ind.Eng.Chem., 59(12), 35 (1967).
41. Martin, J.J., J.Chem.Eng.Data, 5, 334 (1960).
42. Martin, J.J. and Y.C. Hou, A.I.Ch.E.J., 5, 125 (1959).
43. Martin, J.J. and L.F. Albright, Ind.Eng.Chem., 44, 188 (1952).
44. Martin, J.J., "Thermodynamic and Transport Properties of Gases, Liquids, and Solids", Amer.Soc. Mech.Eng., N.Y., 1959, 110 pp.
45. McCullough, J.P., D.R. Douslin, D.W.Scott, and R.T. Moore, J.Am.Chem.Soc., 78, 5457 (1956).
46. McMicking, J.H., and W.B. Kay, 'Vapor Pressure and Saturated Liquid and Vapor Densities of the Isomeric Heptanes and Isomeric Octanes', paper presented at the 30th meeting of the Amer. Pet. Institute Division of Refining, Montreal, Canada,(1956).
47. Michels, A., and T.Wassenaar, Physica, 14, 104 (1948).
48. Michels, A., T. Wassenaar, G.J. Walkers, C. Prins and L.V.D., Klundert, J.Chem.Eng.Data, 11(4), 449 (1966).
49. Michels, A., T.Wassenaar, P. Louwerse, R.J. Lumbeck, and G.T. Walkers, Physica, 19, 287 (1953).
50. Miller, D.G., J. Phys. Chem., 68(6), 1399 (1961).
51. Murphy, K.P., J.Chem.Eng. Data, 9, 259 (1964).

52. Oliver, G.D., J.W. Grisard, and C.W. Cunningham, J.Am.Chem.Soc., 73, 5719 (1951).
53. Osborne, N.S., H.F. Stimson, E.F. Flock, and D.C. Ginnings, J.Res.Natl. Bur.Std., 10, 155 (1933).
54. Patrick, C.R., and G.S., Prosser, Trans.Faraday Soc., 60, 700 (1964).
55. Piacentini, A. and F.P. Stein, Chem.Eng. Prog. Symp. Series, 63 (81), 28, (1967).
56. Porter, F., J.Am.Chem.Soc., 48, 2655 (1926).
57. Ramkrishna, D., Chem.Eng.Sci. (In press).
58. Roland, M., Bull. Soc. Chim., Belg., 37, 117 (1928).
59. Sage, B.H., D.C. Webster, and W.N. Lacey, Ind. Eng. Chem., 29, 1188 (1937).
60. "Selected Values of Properties of Chemical Compounds", Thermodynamics Research Center Data Project, Thermodynamic Research Center, Texas A&M Univ., College Station, Tex. (Loose leaf data sheets extant, 1971).
61. "Selected values of Properties of Hydrocarbons and Related Compounds", American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A&M Univ., College Station, Tex. (Loose-leaf data sheets, extant, 1971).
62. Sharma, D., "Thermodynamic Properties of a Few Pure Component and Mixed Refrigerants", Master's Thesis, Department of Mechanical Engineering, IIT-Kanpur, (1969.).
63. Sinka, J.V., J.Chem.Eng. Data, 15(1), 71 (1970).
64. Sinka, J.V., J.Chem.Eng.Data, 15(1), 73 (1970).
65. Sokolov, V.V., L.P. Zhilina, and K.P. Mishchenko, Z. Prikl. Khim., 36, 750 (1963).
66. Suh, K.W. and T.S. Storvick, A.I.Ch.E. J., 13(2), 231 (1967).

67. Timmermans, J. "Physico Chemical Constants of Pure Organic Compounds, Vol. I, ~~1950~~ . . . . . Publishing Company, Amsterdam, London, N.Y. (1955).
68. Yen, L.S. & S.S. Woods, A.I.Ch.E., J., 12(1), 95, (1966).
69. Yesavage, V.F., D.L. Kata, and J.E. Powers, J. Chem. Eng. Data, 14, 197 (1969).
70. Young, S., Sci. Proc. Soc., Dublin, N.S. XII, 374 (1910).
71. Willingham, C.B., W.J. Taylor, J.M. Pignocco, and F.D. Rossini, J. Res. Natl. Bur. Std., 35, 219 (1945).
72. Zmaczynski, M.A., J. Chim. Phys., 27, 503 (1970).

# APPENDIX 1

## APPLICATION OF LEAST SQUARES ORTHOGONAL POLYNOMIAL FITTING TO ILL CONDITIONED EQUATIONS

The system of equations for which the solution is very sensitive to minute alterations in the coefficients are called ill conditioned. This tiny alteration is brought about by round-off error during computation.

$$\text{Let } y = \sum a_j \phi_j \quad (\text{A-1})$$

be the equation whose coefficients  $a_j$  are to be evaluated by least squares regression analysis.  $a_j$ 's are obtained by minimizing the following function  $f$ .

$$f = \sum_{i=1}^N (y - a_j \phi_j)^2 \quad (\text{A-2})$$

where  $N$  = number of data points

$$\frac{\partial f}{\partial a_j} = \sum_{i=1}^N (y - a_j \phi_j) \phi_j = 0 \quad (\text{A-3})$$

Putting these  $J$  equations in matrix form, we get

$$AX = B \quad (\text{A-4})$$

where  $A$  is defined as

$$A = \begin{bmatrix} \sum_{i=1}^N \phi_1 \phi_1 & \sum \phi_1 \phi_2 & \cdots & \sum \phi_1 \phi_j \\ \sum \phi_2 \phi_1 & \sum \phi_2 \phi_2 & \cdots & \sum \phi_2 \phi_j \\ \cdots & \cdots & \cdots & \cdots \\ \sum \phi_j \phi_1 & \sum \phi_j \phi_2 & \cdots & \sum \phi_j \phi_j \end{bmatrix} \quad (\text{A-5})$$

For  $\phi_j = x^j$  and for large  $N$  (Number of points) and large  $m$

(order of equation) and  $x_i$  are equidistant and varying from 0 to 1, then

$$\frac{1}{N} \sum_{i=0}^N x_i^k \sim \int_0^1 x^k dx = \frac{1}{k+1} \quad (\text{A-6})$$

This leads to

$$A = N \begin{bmatrix} 1 & 1/2 & 1/3 \cdots 1/m+1 \\ 1/2 & 1/3 & 1/4 \cdots 1/m+2 \\ \cdots & \cdots & \cdots & \cdots \\ 1/m+1 & 1/m+2 & 1/m+3 & 1/2m+1 \end{bmatrix} \quad (\text{A-7})$$

This matrix is called Hilbert matrix and causes ill-conditioning.

The geometrical interpretation of ill-conditioning is given as follows:

$$\text{Let } R_1 = a_{11} x + a_{12} y - c_1 \quad (\text{A-8})$$

$$R_2 = a_{21} x + a_{22} y - c_2 \quad (\text{A-9})$$

Then the equations  $R_1=0$  and  $R_2=0$  represent a pair of straight lines intersecting at point P. Suppose, however, we do not demand that  $R_1 = R_2 = 0$  but only that  $|R_1| < e_1$ ,  $|R_2| < e_2$ , where  $e_1$  and  $e_2$  are small positive numbers. Then we only demand that the solution lie in a narrow band (bounded by the lines  $R_1 \pm e_1 = 0$  on either side of  $R_1 = 0$  and in another narrow band (bounded by the lines  $R_2 \pm e_2 = 0$ ) on either side of  $R_2 = 0$ . If the two lines meet at a moderately sharp angle, this gives us an appropriate solution. The coordinates of any point in the shaded parallelogram will be near to those of the true solution P.



If, on the other hand, the two lines in Fig.A-1 ( ) are nearly coincident, then the shaded parallelogram will be extremely long and narrow, and there will be points within it, situated a very great distance from P, which makes  $|R_1| < e_1$  and  $|R_2| < e_2$ .

A generalization of this concept provides us with a possible measure of ill-condition. If  $n=3$ , the equations represent three planes

$$\sum_{i=1}^3 a_{ij} x_j - c_j = 0 \quad (i=1,2,3) \quad (A-10)$$

The angle between any two of them, say the 1st and 2nd is given by:

$$\cos \theta_{12} = a_{11} a_{21} + a_{12} a_{22} + a_{13} a_{23} / ((a_{1j}^2)^{1/2} (a_{2j}^2)^{1/2}) \quad (A-11)$$

Generalising this formula to  $n$  dimensions, we say that  $n$  linear equations represent  $n$  hyperplanes and that the  $\binom{n}{2}$  angles between them are given by

$$\cos \theta_{ij} = \frac{\sum_{k=1}^n a_{ik} a_{jk}}{(\sum_{k=1}^n a_{ik}^2)^{1/2} (\sum_{k=1}^n a_{jk}^2)^{1/2}} \quad (A-12)$$

If certain of the  $\theta_{ij,s}$  are very small, that is the cosines are nearly 1, then the equations are ill-conditioned.

Now let us see how orthogonal property is helpful in avoiding ill-conditioning.

From the orthogonal property.

$$\begin{aligned} \int \phi_j \phi_k W(x) dx &= 0 && \text{if } j \neq k \\ &= 1 && \text{if } j = k \end{aligned}$$

The diagonal elements of coefficient matrix becomes 1 and other elements become zero. This makes the matrix unitary and ill-conditioning is avoided.

Geometrical interpretation can be given as follows. Since planes are orthogonal, they make 90° angle between each other avoiding ill-conditioning as shown above by Eqn.(A-12).

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## APPENDIX 2

### GENERATION OF ORTHOGONAL POLYNOMIALS BY GRAM - SCHMIDT SCHEME

Given linearly independent functions  $1, x, x^2, \dots, x^n$  over a certain interval  $[a, b]$  and a weight function  $W(x)$ , to construct  $\{\phi_n(x)\}_a^b$  where  $\phi_n(x)$  are orthogonal polynomials.

$$(1) \quad \phi_0 = \frac{1}{\|1\|} \quad \text{where} \quad \|1\|^2 = \int_a^b W(x) dx \quad (A-13)$$

(2) determine  $C_0$  such that  $(x - C_0 \phi_0)$  is orthogonal to  $\phi_0$ .

$$((x - C_0 \phi_0), \phi_0) = 0 \quad (A-14)$$

$$\text{or} \quad \int_a^b (x - C_0 \phi_0) \phi_0 W(x) dx = 0 \quad (A-15)$$

$$\text{or} \quad x \phi_0 - C_0 (\phi_0, \phi_0) = 0 \quad (A-16)$$

$$\text{or} \quad C_0 = \frac{(x, \phi_0)}{(\phi_0, \phi_0)} = (x, \phi_0) = \int_a^b x \phi_0 W(x) dx \quad (A-17)$$

$$\phi_1 = \frac{x - C_0 \phi_0}{\|x - C_0 \phi_0\|} \quad (A-18)$$

In general, the process can be continued to yield,

$$\phi_r = \frac{x^r - \sum_{m=0}^{r-1} (x^r, \phi_m) \phi_m}{\|x^r - \sum_{m=0}^{r-1} (x^r, \phi_m) \phi_m\|} \quad (A-19)$$

where  $r$  takes the value of  $1, 2, 3, \dots, r+1$ .

...

TABLE 1: LITERATURE DATA REFERENCES FOR VAPOR PRESSURE

	SOURCES OF VAPOR-PRESSURE DATA	$T_c(39)$ °K	$P_c(39)$ atm.	Calcd. $\Delta H_v$ AT 25°C KCAL MOLE <sup>-1</sup>	Exptal. $\Delta H_v$ AT 25°C KCAL MOLE <sup>-1</sup>	Boiling PT. AT 760 MM N.B.P. °K	Calcd. $\Delta H_v$ AT N.B.P. KCAL MOLE <sup>-1</sup>	Exptal. $\Delta H_v$ AT N.B.P. KCAL MOLE <sup>-1</sup>
70								
Oxygen	32	154.74	50.14	-	-	90.174	1.60	1.630
Water	44,53	647.30	218.30	10.31	-	-	9.76	-
Carbon mono- oxide	14,47	-	-	-	-	-	-	-
Nitrouxide	17,32	-	-	1.40	-	184.671	3.92	3.956
Sulfurdioxide	37	430.7	77.8	-	-	-	-	-
Methane	6,29	190.55	45.44	-	-	111.56	1.92	1.955
Ethane	56	305.43	48.16	0.995	1.20	184.52	3.48	3.517
Propane	12,61	369.82	41.94	3.39	3.605	231.08	4.46	4.487
n-butane	1,34,61	425.16	37.47	4.96	5.03	272.65	5.33	5.352
Isobutane	16,61,69	408.13	36.00	4.49	4.57	261.425	5.02	5.09
n-pentane	9,59,61	469.60	33.25	6.83	6.316	309.223	6.71	6.16
Neo-pentane	9,61	433.75	31.57	5.18	5.205	282.654	5.41	5.438
n-hexane	5,35	507.40	29.3	7.43	7.541	341.283	6.89	6.896
2-3dimethyl- butane	35,61	537.29	28.70	6.88	6.961	331.138	6.48	6.519
2-2-4trimethyl pentane	46,71	543.89	25.34	8.31	8.397	372.387	7.41	7.343
2-3-3-trimethyl pentane	46,71	573.49	27.83	8.60	8.896	387.911	7.68	7.73

(Table 1 continued)

Propane	23, 49	365.00	45.6	3.23	-	225.45	4.38	4.402
1-butene	8, 61	419.6	39.7	4.79	4.81	266.891	5.25	5.238
Isobutene	7, 61	417.89	39.48	4.77	4.92	266.25	5.23	5.286
Benzene	3, 10, 61	562.09	48.34	8.10	8.09	353.247	7.30	7.352
Toluene	3	591.72	40.55	9.47	9.08	383.773	8.01	7.931
O-xylene	3, 25	630.20	36.84	13.51	-	417.54	8.69	8.80
Methanol	4, 60	512.58	79.9	8.96	8.946	337.85	8.67	8.433
n-butanol	4, 60	562.93	43.55	14.78	-	390.81	10.30	10.31
Isobutanol	4, 60	547.73	42.39	13.65	12.23	390.809	9.76	10.07
Acetone	38, 58, 64, 71	508.2	46.40	7.94	-	-	-	-
Methylethyl Ketone	15, 38	535.6	41.0	8.67	-	352.717	7.69	7.57
Methyl n-propyleketone	15, 38	564.0	38.4	-	-	-	-	-
Diethylketone	15, 38	561.6	36.9	11.66	-	375.116	8.27	8.06
Acetic acid	70	594.45	57.1	-	-	-	-	-
Methylformate	70	487.2	59.2	6.86	-	304.96	6.76	6.741
Ethylformate	70	508.4	46.8	8.48	-	327.56	7.12	7.178
n-propyl-formate	70	538.0	40.1	-	-	-	-	-
diethylether	36	466.70	35.9	6.48	6.51	-	-	-

Table 1 (continued)

Perfluoro-n-propane	18	345.0	26.45	3.36	-	236.811	4.75	4.752
Perfluoro-n-heptane	50	-	-	-	-	-	-	-
Perfluoro-2-methylpentane	18	-	-	-	-	-	-	-
Perfluoro-cyclobutane	19, 26	-	-	4.89	-	267.245	5.53	5.5
Pentafluoro-benzene	2, 24, 54	532.0	34.7	9.00	-	-	-	-
Fluorobenzene	45	569.09	44.91	8.06	-	-	-	-
Pentafluoro chlorobenzene	2.24	571.0	31.8	9.74	-	-	-	-
Dichlorodifluoro-methane	67	384.7	38.671	3.84	-	243.55	4.74	-
Ethylchloride	11, 28	460.4	52.0	5.71	-	-	-	-
Pentafluoro-chloroacetone	51	-	-	-	-	-	-	-
Dichlorotetrafluoroethane	41	418.8	32.2	-	-	-	-	-
Propylchloride	11	503.0	45.2	7.02	-	-	-	-
Trifluorochloroethylene	52	-	-	-	-	-	-	-
Hexafluoro acetone	51	357.2	28.0	-	-	-	-	-

TABLE 2: CONSTANTS OF EQUATION (39)

Compound	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>
Oxygen	-5.20	-8326.3453	57666.972	69214.515	28961.155
Water	-8.60	12793982.0	-27418730.0	21245304.0	-5435268.3
Carbon Mono oxide	-6.00	22546.278	7375.4516	-40164.122	24185.991
Nitrous Oxide	-7.50	1205249.8	-2501878.3	1904072.0	-477988.06
Sulfur dioxide	-6.20	-128463.14	519422.15	-569062.94	216502.05
Methane	-5.00	-6132.4356	39227.913	-45553.473	19202.423
Ethane	-7.50	2226843.6	-6410644.4	6602821.3	-2335917.6
Propane	-6.50	-16701.358	218454.45	-303628.54	129853.24
n-butane	-6.00	-41334.539	177693.09	-196924.44	75612.854
Iso-butane	-6.00	35675.560	161331.12	-181701.39	70600.589
n-pentane	-8.00	875928.36	1742572.5	1263375.0	298290.57
Neo-pentane	-7.00	-7858.9971	284466.33	-436129.09	194210.78
n-Hexane	-8.00	197766.34	286805.12	-847150.35	450931.38
2,3-dimethylbutane	-7.00	74666.64	456340.45	-589334.57	241380.96
2,2,4-trimethylpentane	-8.60	1597515.7	3241146.9	2273933.9	-492606.67
2,3,3-trimethylpentane	-8.00	281550.23	-44882.149	-450611.05	297016.95
Propene	-6.00	-36653.254	191068.53	-225375.15	89284.313
Isobutene	-6.00	-41150.496	180254.27	-200743.55	77561.937

(Table 2 continued)

Compound	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>
1-butene	-6.00	-46155.886	200512.02	-225991.94	87600.584
Benzene	-6.00	-62149.596	254900.47	-279580.61	106303.91
Toluene	-9.30	236218.82	-68912807.0	69751494.0	-24027929.0
O-xylene	-6.00	-39932.816	144304.49	-141992.59	52425.017
Methanol	-9.10	798301.55	2357624.4	-4488476.1	2046717.2
n-butanol	-9.00	4783554.5	18173120.0	-20652114.0	7616777.4
Isobutanol	-9.00	-4800946.6	18164711.0	-20591998.0	7572681.2
Acetone	-6.00	-79817.525	294845.74	-318623.06	122269.88
Methylethylketone	-7.00	-287306.55	1171572.1	-1369285.7	529921.47
Methyl-n-propylketone	-5.00	15314.628	49949.478	-50628.341	21650.816
Diethylketone	-6.60	-177379.27	660405.15	-730174.92	274296.01
Acetic acid	-8.00	-50958.566	1006959.9	-1352373.6	566946.98
Methyl formate	-6.80	224329.78	1008826.7	-1200227.8	469004.25
Ethyl formate	-8.30	1277100.4	-1765531.0	476440.95	200233.04
n-propyl formate	-7.00	244149.31	1024900.1	-1207737.5	471003.14
Diethyl ether	-7.00	133350.90	641666.34	-773141.82	304341.51
Perfluro-n-propane	-7.00	-102286.03	445328.47	-504578.05	190440.70
Perfluro-2-3 dimethyl butane	-7.00	-145572.12	537614.52	-593164.69	222323.36



(Table 2 continued)

Compound	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>
Perfluro-n-heptane	-7.00	73512.631	245216.69	-240516.24	86267.887
Perfluro-cyclobutane	-9.00	2734811.6	-5538364.7	3848000.2	-820699.36
Pentaflurobenzene	-9.00	35159949.0	-96607104.0	92250766.0	-30049493.0
Flurobenzene	-7.00	-122652.16	717905.36	-925730.38	379768.89
Pentaflurochloro- benzene	-8.30	-531610.008	3300539.7	-4484564.6	1897511.0
Diflurodichloro- methane	-5.00	-9347.6317	32979.622	-26721.751	9463.4958
Ethylchloride	-7.40	384649.55	-421010.06	2016.4023	119127.23
Pentaflurochloro- acetone	-7.00	-160071.30	-649546.40	741515.76	283310.92
Dichlorotetrafluro- ethane	-6.00	-49615.384	193138.10	-212532.15	32043.632
Propylchloride	-7.00	-142001.04	776030.51	-956500.97	370398.53
Triflurochloroethylene	-8.60	6884093.1	-19612014.0	-19774622.0	-6835462.9
Hexafluroacetone	-7.00	176723.55	688750.25	-772279.65	291031.41
Perfluro-3-methyl- pentane	-8.00	-293311.47	1193350.2	-1352357.0	501772.39
n-Hexadecafluro- heptane	-7.00	-73512.631	245216.69	-240516.24	86267.887

TABLE 4: COMPARISON OF THE PROPOSED EQUATION  
WITH OTHER EQUATIONS

Compound	Proposed Eqn.		Martin Eqn. (44)		IIT-K Eqn. (27)	
	Av. Dev.	Std. Dev.	Av. Dev.	Std. Dev.	Av. Dev.	Std. Dev.
Oxygen	.016	.0018	.021	0.007	.016	.0055
Water	.054	.0073	.074	.0194	.091	.0194
Carbon monoxide	.005	.00005	-	-	-	-
Nitrous oxide	.011	.0003	.017	.0035	.019	.0040
Sulfur dioxide	.031	.0020	-	-	-	-
Methane	.008	.0002	.007	.0016	.018	.0054
Ethane	.022	.0015	.016	.0056	.009	.0026
Propane	.043	.0044	.169	.0349	.125	.0213
n-butane	.018	.0011	.031	.0105	.031	.0106
Isobutane	.005	.0001	.004	.0025	.010	.0045
n-pentane	.031	.0029	.040	.0107	.028	.0079
neopentane	.008	.0002	.011	.0052	.007	.0031
n-hexane	.011	.0004	.007	.0015	.013	.0029
2,3 dimethylbutane	.011	.0003	.025	.0079	.017	.0057
2,2,4methylpentane	.006	.0001	.015	.0048	.011	.0026
2,3,3trimethylpentane	.004	.00003	.010	.0036	.004	.0013

(Table 4 continued)

Compound	Proposed Eqn.		Martin Eqn. (44)		IIT-K Eqn. (27)	
	Av. Dev.	Std. Dev.	Av. Dev.	Std. Dev.	Av. Dev.	Std. Dev.
Propane	.017	.0009	.052	.0207	.032	.0128
1-butene	.002	.00003	.007	.0041	.009	.0041
Isobutene	.003	.0001	.014	.0037	.010	.0030
Benzene	.007	.0004	.028	.0110	.016	.0056
Toluene	.023	.0017	.014	.0053	.012	.0058
O-Xylene	.004	.0001	.005	.0027	.004	.0020
Methanol	.0261	.0017	.065	.0249	.035	.0113
n-butanol	.012	.0004	.011	.0030	.017	.0042
Isobutanol	.013	.0004	.019	.0050	.022	.0051
Acetone	.024	.0014	.038	.0099	.028	.0068
Methylethylketone	.018	.0006	.061	.0156	.039	.0076
Methyle-n-propyl ketone	.040	.04	.053	.012	.043	.008
	.040	.040	.053	.0120	.043	.0089
Diethylketone	.022	.022	.053	.0124	.046	.0083
Acetic acid	.045	.045	-	-	-	-
Methylformate	.046	.046	.056	.0156	.034	.0091
Ethylformate	.010	.010	-	-	-	-
n-propyl formate	.009	.0002	.012	.0044	.018	.0065

(Table 4 continued)

Compound	Proposed Eqn.		Martin Eqn. (44)		IIT-K Eqn. (27)	
	Av. Dev.	Std. Dev.	Av. Dev.	Std. Dev.	Av. Dev.	Std. Dev.
Diethyl ether	0.01	.0003	.007	.0027	.020	.0066
Perfluro-n-propane	.008	.0001	.014	.0049	.022	.0084
Perfluro, 2,3-dimethyl butane	.014	.0006	.014	.0061	.049	.0198
Perfluro-n-heptane	.009	.0002	.004	.0014	.023	.0061
Perfluoro-cyclobutane	.039	.0044	.015	.0059	.003	.0030
Penta flurobenzene	.037	.0049	.036	.0126	.045	.0165
Flurobenzene	.011	.0004	.012	.0031	.009	.0026
Pentaflurochlorobenzene	.021	.0010	.018	.0046	.027	.0035
Di fluoro dichloromethane	.006	.0001	.010	.0041	.006	.0021
Ethylchloride	.043	.0043	.056	.0170	.069	.0225
Pentaflurochloracetone	.009	.0001	.042	.0158	.036	.0108
Dichlorotetrafluroethane	.050	.0059	.044	.0135	.052	.0157
Propylchloride	.039	.005	.032	.0102	.152	.0583
Trifluoroethylen	.071	.0126	.092	.0316	.076	.0262
Hexafluroacetone	.010	.0001	.011	.0038	.014	.0056
n-hexadecafluroheptane	.009	.0002	-	-	-	-

TABLE 5

## SOURCE OF DATA

S.No.	Compound	Authors	Temp. range °C	Pressure range	Vapor Pressure Data	$\Delta H_v$	Liquid Density	C <sup>o</sup> p
1.	CH <sub>3</sub> Cl	Hsu & McKetta (33)	25-400	1-100 atm	Hsu & McKetta (33)	Calcd.	Yen & Wood (68)	TRC Table (60)
2.	CF <sub>2</sub> Cl <sub>2</sub>	Michels (47)	50-150	7-85 atm	Timmermans (67)	"	"	"
3.	CF <sub>3</sub> Cl	Michels (47)	30-150	1-100 atm	Martin (43)	"	"	"
4.	CFClH <sub>2</sub> + C <sub>2</sub> F <sub>3</sub> Cl <sub>2</sub> H	Sinka (63)	100-250	15-70 atm	Sinka (63)	"	Sinka (63)	"
5.	CF <sub>3</sub> Cl + CF <sub>3</sub> H	Sinka (64)	20-200	15-70 atm	"	"	" (64)	"

TABLE 6

DATA USED FOR THE CALCULATION OF THERMODYNAMIC PROPERTIES

COMPOUND: Methyl Chloride ( $\text{CH}_3\text{Cl}$ )

(1) Critical Constants:

$$T_c = 416.15^\circ\text{K} ; P_c = 65.9 \text{ atm.} ; v_c = 0.143 \text{ litre gm.mole}^{-1}$$

(2) Constants of Martin-Hou Equation of State: (Calculated by us)

$$A_2 = -0.99141179 \times 10 \quad B_2 = 0.10223509 \times 10^{-1} \quad C_2 = -0.2779375 \times 10^3$$

$$A_3 = -0.15191194 \quad B_3 = 0.80124886 \times 10^{-3} \quad C_3 = 0.13616686 \times 10^3$$

$$A_4 = -0.53981769 \times 10^{-1} \quad B_4 = 0.11809086 \times 10^{-3} \quad C_4 = 0.11110276 \times 10^2$$

$$A_5 = 0.58684501 \times 10^{-2} \quad B_5 = -0.12064974 \times 10^{-4} \quad C_5 = 0.20026005$$

$$b = 0.004 \text{ litre mole}^{-1} \quad k = 5.475 \quad R = 0.082056 \frac{\text{litre atm}}{^\circ\text{K mole}}$$

average deviation = 0.4%

(3) Vapor Pressure Equation (33)

$$\log P = -6.2777215 - \frac{650.82895}{T} + 3.7672565 \log T \\ - 0.11995288 \times 10^{-4} \times T^2$$

(4) Heat Capacity ( $C_p$ ) Equation

$$C_p = \frac{1370.879}{T} - 4.3414333 + 0.40522185 \times 10^{-1} \times T \\ - 0.24222874 \times 10^{-4} \times T^2 - \frac{0.52130329 \times 10^5}{T^2} - 0.10767405 \times 10^6 \times T^3$$

Average percentage deviation = 0.21%

(5) Liquid density calculated from Yen and Woods (68).

TABLE 7

DATA USED FOR THE CALCULATION OF THERMODYNAMIC PROPERTIES

COMPOUND: Difluorodichloromethane ( $\text{CF}_2\text{Cl}_2$ )

1. Critical Constants (39)

$$T_c = 384.7^\circ\text{K} \quad P_c = 38.671 \text{ atm} \quad v_c = 0.217 \text{ lit.g.mole}^{-1}$$

2. Constants of Martin-Hou Equation of State (calculated by us)

$$A_2 = -0.11713538 \times 10^2 \quad B_2 = 0.13384294 \times 10^{-1}$$

$$C_2 = -0.14949738 \times 10^3 \quad A_3 = 0.6770087$$

$$B_3 = -0.81274894 \times 10^{-4} \quad C_3 = -0.13910429 \times 10^3$$

$$A_4 = -0.19041529 \quad B_4 = 0.21623801 \times 10^{-3}$$

$$C_4 = 0.64101192 \times 10^2 \quad A_5 = 0.41118244 \times 10^{-2}$$

$$B_5 = 0.12294899 \times 10^{-4} \quad C_5 = -0.55337002 \times 10$$

$$b = 0.002 \text{ lit./mole} \quad k = +5.475 \quad R = 0.082056 \frac{\text{lit.atm.}}{^\circ\text{K mole}}$$

3. Vapor Pressure Equation: (fitted by us)

$$P = \text{Exp}(-5/T_r) \times (-9847.6317 + 32979.692 \times T_r - 26721.751 \times T_r^2 + 9463.4958 \times T_r^3)$$

$$\text{Average deviation} = 0.00845 \text{ atm}$$

$$\text{Standard deviation} = 0.0001$$

4. Heat Capacity Equation: (fitted by us)

$$C_p = \frac{-2559.9}{T} + 21.0474 + 0.15074 \times 10^{-1} \times T - 0.12915 \times 10^{-4} \times T^2 + \frac{0.12616 \times 10^6}{T^2} + 0.36216 \times 10^{-8} \times T^3$$

$$\text{Average deviation} = 0.1\%$$

5. Liquid density calculated from Yen and Woods(68)

correlation.

TABLE 8

DATA FOR THE CALCULATION OF THERMODYNAMIC PROPERTIES

COMPOUND: Trifluorochloromethane ( $\text{CF}_3\text{Cl}$ )

Critical Constants

$$T_c = 379^\circ\text{K} \quad P_c = 40 \text{ atm} \quad v_c = 0.19 \text{ lit.g.mole}^{-1}$$

Constants of Martin Hou Equation of State:(calculated by us)

$$\begin{aligned} A_2 &= -0.89171521 \times 10 & B_2 &= 0.11677829 \times 10^{-1} & C_2 &= -0.12604563 \times 10^3 \\ A_3 &= -0.66368465 & B_3 &= 0.27641571 \times 10^{-3} & C_3 &= -0.73918369 \times 10 \\ A_4 &= -0.12507003 & B_4 &= 0.11943893 \times 10^{-4} & C_4 &= 0.14352154 \times 10^2 \\ A_5 &= 0.11562561 \times 10^{-1} & B_5 &= -0.17963301 \times 10^{-5} & C_5 &= -0.17967315 \times 10 \\ b &= 0.001 \text{ lit./mole} & k &= 5.475 & R &= 0.082056 \frac{\text{litre atm.}}{^\circ\text{K mole}} \end{aligned}$$

Average deviation = 0.1%

Vapor Pressure Equation (43)

$$\log_{10} P(\text{psia}) = 36.7613 - \frac{2623.988}{T} - 11.80586 \times \log_{10} T + 5.71495 \times 10^{-3} \times T$$

T in  $^\circ\text{K}$

Heat Capacity Equation (fitted by us)

$$\begin{aligned} C_p &= \frac{-0.67384471 \times 10^4}{T} + 32.84375 - 0.2628254 \times 10^{-2} \times T \\ &\quad - 0.35650056 \times 10^{-6} \times T^2 + \frac{581926.12}{T^2} + 0.33124984 \times 10^{-9} \times T^3 \end{aligned}$$

Average deviation = 0.1%

Liquid density calculated from Yen and Woods(68) correlation.



TABLE 9

DATA USED FOR THE CALCULATION OF THERMODYNAMIC PROPERTIES

COMPOUND: Azeotropic mixture of  $\text{CFClH}_2$  (55.1%) +  $\text{C}_2\text{F}_4\text{Cl}_2$

Critical Constants(63)  $T_c = 415.2^\circ\text{K}$   $P_c = 749 \text{ psia}$

$$\rho_c = 0.539 \text{ gm/cc}$$

Constants of Martin-Hou Equation of State (63)

$$\begin{aligned} A_2 &= -0.2351595 \times 10^5 & B_2 &= 0.2302919 \times 10^2 & C_2 &= -0.3169159 \times 10^6 \\ A_3 &= 0.3111256 \times 10^5 & B_3 &= -0.2750807 \times 10^2 & C_3 &= 0.5292572 \times 10^6 \\ A_4 &= -0.1575132 \times 10^5 & B_4 &= 0.0 & C_4 &= 0.0 \\ A_5 &= -0.325344 \times 10^4 & B_5 &= 0.201258 \times 10^2 & C_5 &= -0.1332969 \times 10^6 \\ b &= 0.3777405 \text{ cc/gm} & k &= 5.475 & R &= 0.1287070 \times 10^2 \frac{\text{cc psia}}{^\circ\text{K gm.}} \end{aligned}$$

Vapor pressure equation (63)

$$\log P (\text{Psia}) = 8.312656 - \frac{0.147347 \times 10^4}{T} - 0.771637 \times 10^{-2} T + 0.761974 \times 10^{-5} T^2$$

Heat Capacity Equation (fitted by us)

$$\begin{aligned} C_p (\text{CFClH}_2) &= \frac{-0.46281776 \times 10^4}{T} + 17.978793 + 0.10870963 \times 10^{-1} \times T \\ &\quad - 0.5347892 \times 10^{-5} T^2 + \frac{0.53216935 \times 10^6}{T^2} + 0.98639508 \times 10^{-9} T^3 \end{aligned}$$

Average deviation = 0.1%

$$\begin{aligned} C_p (\text{C}_2\text{F}_4\text{Cl}_2) &= \frac{-0.14072425 \times 10^5}{T} + 58.338731 - 0.75226658 \times 10^{-2} T \\ &\quad - 0.27010826 \times 10^{-6} T^2 + \frac{1386029.2}{T^2} + 0.94739429 \times 10^{-9} T^3 \end{aligned}$$

Average deviation = 0.1%

Saturated Liquid Density (63)

$$\begin{aligned} D(\text{gm/cc}) &= 0.5391 + 0.569272 \times (1-T_r)^{1/3} + 1.48902 \times (1-T_r)^{2/3} \\ &\quad - 1.64833 \times (1-T_r) + 0.988902 \times (1-T_r)^{4/3} \end{aligned}$$

TABLE 10

DATA USED FOR THE CALCULATION OF THERMODYNAMIC PROPERTIES

COMPOUND: Azeotropic mixture of  $\text{CF}_3\text{Cl}$  (50%) and  $\text{CF}_3\text{H}$  (50%)

Critical Constants (64)

$$T_c = 292.6^\circ\text{K} ; \quad P_c = 43.00 \text{ atm}; \quad \rho_c = 0.564 \text{ gm/cc}$$

Constants of Martin-Hou Equation of State (64)

$A_2 = -9.8902899 \times 10^2$	$B_2 = 1.2327089$	$C_2 = -1.8509064 \times 10^4$
$A_3 = 1.0968311 \times 10^3$	$B_3 = -1.0625844$	$C_3 = 2.9079090 \times 10^2$
$A_4 = -5.8622059 \times 10$	$B_4 = 0.0$	$C_4 = 0.0$
$A_5 = -5.8740372 \times 10$	$B_5 = 0.8136030$	$C_5 = -6.4500245 \times 10^3$
$b = 0.3440809 \text{ cc/gm}$	$k = 5.475$	$R = 0.94056886 \frac{\text{cc atm}}{^\circ\text{K gm}}$

Vapor Pressure Equation (64)

$$\log_{10} P = 8.48908 - \frac{1.143932 \times 10^3}{T} - 1.66749 \times 10^{-2} \times T + 2.25561 \times 10^{-5} \times T^2$$

Heat Capacity Equation

$$C_p (\text{CF}_3\text{Cl}) = \frac{-0.39449772 \times 10^4}{T} + 32.84375 - 0.2628254 \times 10^{-2} T - 0.35650056 \times 10^{-6} \times T^2 + \frac{0.52474373 \times 10^6}{T^2} + 0.33124984 \times 10^{-8} \times T^3$$

$$C_p (\text{CF}_3\text{H}) = \frac{-0.67384471 \times 10^4}{T} + 12.851214 + 0.18676057 \times 10^{-1} \times T - 0.1023215 \times 10^{-1} \times T^2 + \frac{0.58192612 \times 10^6}{T^2} + 0.21034459 \times 10^{-8} \times T^3$$

Saturated liquid density (64)

$$\rho(\text{gm/cc}) = 0.5640 + 1.2802 \times (1-T_r)^{4/3} - 1.6817 \times (1-T_r)^{2/3} + 4.4210 \times (1-T_r) - 2.9158 \times (1-T_r)^{4/3}.$$

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TABLE 11  
COMPARISON OF OUR VALUES BY-DUPONT VALUES

T in °K	P atm.	$V_g$ Lit/mol	OBS $V_g$	H Kcal/mol	OBS H	H Kcal/mol°K	OBS S
$CH_2Cl$							
270	1.070	20.0	18.5	5.875	5.8000	0.0233	0.0230
300	4.458	5.0	5.9	6.000	5.980	0.0211	0.0210
400	6.280	5.0	5.8	7.169	7.100	0.0233	0.0235
450	17.04	2.0	2.1	7.640	7.700	0.0235	0.0230
$CF_2Cl_2$							
250	1.00	20.0	20.10	5.257	5.30	0.0216	0.0217
350	12.33	2.0	2.20	6.718	6.79	0.0222	0.0231
300	2.92	8.0	8.50	6.042	6.10	0.0235	0.023
400	26.27	1.0	1.03	7.46	7.50	0.0231	0.0236
450	11.67	3.0	3.1	8.850	8.9000	0.0274	0.028
$CF_3Cl$							
270	9.48	2.0	1.8	2.287	2.280	0.008	0.0075
300	20.9	0.9	1.1	2.541	2.540	0.0079	0.0076
400	15.42	2.0	2.1	4.578	4.560	0.0143	0.0139
450	11.92	3.0	3.1	5.6000	5.601	0.017	0.017